

**Novel toolkit for post-production quality assurance of
solid recovered fuel (SRF): A focus on sub-sampling
uncertainty and composition identification**

Spyridoula Gerasimidou

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Declaration

The candidate confirms that the work submitted is their own, except where work which has formed part of jointly authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

1. The work in Chapter 2 (Sections 2.2, 2.4.3, 2.5.1.1, and 2.5.2.2), Chapter 4 (Section 4.1.1), Chapter 5 (Section 5.1), and Chapter 6 (Section 6.1) of the thesis has appeared in publication as follows:

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I was responsible for the majority of the work including conceptualisation, methodology, software utilisation, formal analysis, investigation, data collection and curation, writing original draft, visualisation.

The contribution of the other authors was: i) Velis, C. A: supervision, conceptualisation, project administration, resources, critical revision and final approval for submission; ii) Williams, P. T.: supervision, conceptualisation and critical revision; iii) Castaldi, M. J.: conceptualisation and critical revision (expert in waste to energy and thermal recovery processes); iv) Black, L.: critical revision (expert in environmental aspects of cement); and v) Komilis, D.: critical revision and methodology (expert in waste management and statistics).

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Spyridoula Gerasimidou

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Abstract

The inherent heterogeneity of waste-derived products is a key limiting factor for sustainable resources recovery and wider circular economy – also for solid recovered fuels (SRF). Confidence in SRF trading necessitates the manufacture of quality-assured SRF. Herein, a novel and adaptable toolkit for SRF characterisation was established through statistically designed experiments (DoE), applicable for quality assurance (QA) to both SRF producers (post-production) and end-users (pre-recovery). A novel machine learning (ML) SRF composition model was devised, able to identify prevalent polymers (cellulose, xylan, lignin, HDPE, PP, PET, and PVC), by implementing thermogravimetric (TG-DTG) and spectroscopic (FTIR) techniques (Objective 4: O4). Following an optimal mixture design, the applicability of the ML model was verified using synthetic mixtures that resemble SRF (cross-validation), waste mixtures with known composition featuring impurities (hold-out validation), and commercially produced SRF samples. The uncertainty arising from laboratory sub-sampling, expressed as relative standard deviation (RSD), was quantified for key quality properties: moisture (RSD: 2.6%), ash (RSD: 6.1%), calorific (RSD: 4.2%), and chlorine (RSD: 18.2%) content, and thermal stability via TG-DTG (RSD: 32.2%) (O3). Uncertainty was quantified through DoE (balanced nested-ANOVA) under a relatively unbiased, yet affordable and practicable sub-sampling plan, benefiting from state-of-the-art equipment, theoretical calculations according to theory of sampling (ToS), and implementation of best sub-sampling practices (O2). This work (O2&3) led to an integrated and practical characterisation scheme, ensuring the validity of any analytical determination based tool, such as the new ML model. A systematic review explored the variability of chlorine in SRF (key QA property) during SRF pre- and co-processing in cement kilns (main end-user) (O1), informing a tolerable level of Cl variability. This research offers the means to obtain a comprehensive set of information on SRF quality with relatively high confidence and low effort; also bearing far reaching wider implications for solid waste characterisation/ waste-derived products QA.

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“To stand on this step you must be in your own right a member of the city of ideas” Constantine Cavafy

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Nomenclature

AE	Analytical error
ANOVA	Analysis of variance
BAT	Best Available Techniques
BC	Bomb calorimetry
BS	British standard
C&IW	Commercial and industrial waste
CEAP	Circular Economy Action Plan
CEN	European Committee for Standardization
CDW	Construction and demolition waste
CKD	Cement kiln dust
CO ₂ e	Carbon dioxide equivalent
CRM	Certified reference materials
CS	Current sub-sampling plan
CSE	Correct sampling error
DE	Delimitation Error
d.f.	Degrees of freedom
DoE	Design of experiment
DTG	Derivative thermogravimetry
EA	Elemental analyser
EE	Extraction Error
ECOS	European Environmental Citizens Organisation for Standardisation
EGA	Evolved gas analysis
ERFO	European Recovered Fuel Organisation
EU	European Union
FDS	Fraction design space
FE	Fundamental error
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GHG	Greenhouse gas
GSE	Grouping Segregation Error
HHV	Higher heating value
HOV	Homogeneity of variance
IBA	Incinerator bottom ash

IC	Ion chromatography
ICP	Inductively coupled plasma
ICP-SFMS	Inductively coupled plasma-sector field mass spectrometry
IQR	Interquartile range
ISE	Incorrect sampling error
LCI-UCI	Lower and upper confidence interval
LoD	Limit of detection
MAE	Mean absolute error
MAPE	Mean absolute percentage error
MC	Moisture content
MCP	Material, component and product
MdAE	Median absolute error
ML	Machine learning
MRF	Multivariate random forest
MS	Mass spectrometry
MSE	Mean squared error
MSW	Municipal solid waste
MT/MBT	Mechanical treatment/ mechanical-biological treatment
NCV	Net calorific value
NIR	Near infra-red
NS	Sub-sampling without shredding
PA	Polyamide
PE	Preparation error
PC	Principal component
PCA	Principal components analysis
PRISMA	Preferred Reporting Items for Systematic Reviews and Meta-Analyses
PS	Sub-sampling with only primary shredding
PSD	Particle size distribution
PTEs	Potentially toxic elements
QA	Quality assurance
QC	Quality control
QMS	Quality management system
QUOVADIS	Quality Management Organisation, Validation of Standards, Developments and Inquiries for Solid-Recovered Fuels
R ²	Coefficient of determination

RDF	Refuse derived fuel
RHI	Renewable Heat Incentive
RMSE	Root mean squared error
RQ	Research question
RRSE	Root relative squared error
RSD	Relative standard deviation
SBR	Styrene-butadiene rubber
SDM	Selective dissolution method
SE	Sub-sampling error
SFC	Schoeniger flask combustion
SI	Supporting information
SMAPE	Symmetric mean absolute percentage error
SRF	Solid recovered fuel
STA	Simultaneous thermal analysis
TGA	Thermogravimetric analysis
TG-DTG	Thermogravimetric analysis combined with the derivative of TGA signal
ToS	Theory of sampling
Total [Cl]	Concentration of total chlorine content
Total RSD	Total sub-sampling uncertainty
WDF	Waste derived fuel
WP	Work packages
WSM	Weighed sum method
WtE	Waste to energy
w/w	Weight fraction on a wet basis
w/w _d	Weight fraction on a dry basis

List of Symbols and Compounds

Symbols

a_L	Decimal proportion of analyte in the sample
c	Mineralogical factor
C	Sampling constant
d	Particle size

f	Shape factor
FE	Fundamental Error
g	Granulometric factor
<i>l</i>	Liberation factor
M _s	Mass of the sample [g]
Ms	Mass spectrometry
R	Recovery of Total [Cl]
s_{FE}^2	Variance of fundamental error
S	Combustibility index
SS	Sum of squares
T _e	Endset temperature
T _o	Onset temperature
T _p	DTG peak temperature
λ _g	Density of sample
λ _M	Density of analyte

Chemical compounds

ABS	3,3-diphenyl-1-propanamine
Ca	Calcium
CaCO ₃	Calcium carbonate
Ca ₂ (SiO ₄) ₃ (Cl) ₂	Chlorellestadite
CaCl ₂	Calcium chloride
CaO	Calcium oxide (free lime)
CG	Carbonyl dichloride (Phosgene)
Cl	Chlorine
Cl ₂	Molecular chlorine
ClO ⁻	Hypochlorite
ClO ₂	Chlorine dioxide
CPE	Chlorinated polyethylene
C ₂ S	Belite
C ₃ S	Alite
DCM	Dichloromethane
EDC	Dichloroethane
EPI	Epichlorohydrin
Fe	Iron

FeCl ₂	Ferrous chloride
FeCl ₃	Ferric chloride
Fe(OH) ₃	Ferric hydroxide
Fe ₂ O ₃	Ferric oxide or hematite
HCl	Hydrogen chloride
HDPE	High-density polyethylene
Hg	Mercury
H ₂ O	Water
KCl	Potassium chloride
K ₂ Ca ₂ (SO ₄) ₃	Calcium-langbeinite
KOH	Potassium hydroxide
K ₂ O	Potassium oxide
LDPE	Low density polyethylene
MCl ₂	Metal chloride
MgCl ₂	Magnesium chloride
MO	Metal oxide
NaCl	Sodium chloride
NaClO	Sodium hypochlorite
Na ₂ O	Sodium oxide
NaOH	Sodium hydroxide
Na ₂ SO ₄	Disodium sulphate
NH ₄ Cl	Ammonium chloride
O ₂	Molecular oxygen
Pb	Lead
PBT	Polybutylene terephthalate
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzo-p-furans
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PPVC	Plasticized polyvinylchloride
PS	Polystyrene
PVC	Polyvinyl chloride
PVdC	Polyvinylidene chloride
SO ₂	Sulphur dioxide

SO ₃	Sulphur trioxide
SiO ₂	Dioxosilane (silica)
TCE	Tetrachloroethene
TiCl ₃	Trichlorotitanium
VCM	Chloroethene

1 INTRODUCTION

As waste generation has continuously increased over recent years, the need to develop more sustainable waste management systems has been highlighted by many researchers (Iacovidou et al., 2017a; Astrup et al., 2009a; Seadon, 2010). According to a World Bank Group's report, the global solid waste generation is expected to be increased by 70% from 2016 to 2050, due to continuing global urbanisation and population growth (Kaza et al., 2018). In Europe, current municipal solid waste (MSW) generation is 480 kg/ per capita annually (Eurostat, 2018).

This situation has driven to the concept of circular economy based on the development of a new sustainable model where resources are retained in the system for as long as possible and therefore the value recovery from materials, components and products (MCP) is promoted by circulating in closed loops (Iacovidou et al., 2017a). The circular economy aims to disconnect the economic development and human well-being with the increasing consumption of natural resources and the related environmental implications (Hickman, 2000). In many countries, waste management policy is moving from the linear value chain towards more sustainable models by curbing growth in waste generation and increasing the recovery of resources from waste (Hinkel et al., 2019; Iacovidou et al., 2017a). For example, the renewable heat incentive (RHI) that promotes the use of carbon-rich residues as fuel (Kepp and McKendry, 2011).

Waste-to-energy (WtE) processes aim to recover energy content from technically and economically non-recyclable flows, supplementing systems that prioritise recycling (ERFO, 2019; Iacovidou et al., 2018). From that perspective, WtE processes can contribute actively and considerably to reaching the goals of waste management sustainability (Brunner and Rechberger, 2015). Current waste sorting technologies, cross-contamination of recyclable materials such as food plastic packaging, the presence of impurities in plastic waste such as coloured plastic and non-plastic products (accounted for 38% w/w of plastic waste (Faraca and Astrup, 2019)), and the difficulty in separating the recyclable components of multi-material components such as food and drinks cartons, mean that 100% reclamation rate for recycling is an unattainable goal (Rousta et al., 2017; ERFO, 2010; Faraca and Astrup, 2019). In 2016, 31% of post-consumer plastic waste was recycled and 42% went to WtE in Europe (PlasticsEurope, 2018). A recent study investigated the overall recycling potential of plastic

waste based on material flow analysis at Danish recycling centres, reporting that the recyclability of plastic waste ranged from 52-79% depending on its quality, level of impurity and polymer type (Faraca and Astrup, 2019). In addition to this, the comparable energy content of waste derived fuels (WDF) (ca. 15-29 MJ kg⁻¹) with that of coal (ca. 27-31 MJ kg⁻¹) (Seo et al., 2010; Azam et al., 2019) represents a considerable opportunity for a more low-carbon and resource-efficient economy (IEA, 2012).

In 2015, the European Commission adopted the Circular Economy Action Plan (CEAP) aimed to reduce waste generation and increase recycling rates (European Commission, 2015). The role of WtE processes in the circular economy was specified two years later (European Commission, 2017). Specifically, the European Commission stated that WtE processes could assist with the transition to a circular economy as long as the Waste Hierarchy is applied. Therefore, WDF only be produced from residual solid waste that has undergone reclamation for recycling and composting (Samolada and Zabaniotou, 2014; Martignon, 2020).

Solid recovered fuel (SRF) and refuse-derived fuel (RDF) are two major routes to recover energy resources from currently unrecyclable fractions of MSW (Velis et al., 2010). The difference between SRF and RDF is described in **Section 2.1**. SRF, a fuel with specified composition, can be used for replacing fossil fuels in cement kilns (Hinkel et al., 2019). The exact role played by SRF in a circular economy depends on the relationship between public private partnerships, SRF producers and municipalities (Hinkel et al., 2019; Martignon, 2020).

SRF application can offer several environmental and financial benefits including: contribution markedly to the reduction of carbon dioxide equivalent (CO₂e) emissions due to partial carbon neutrality (Garg et al., 2007; Astrup et al., 2009b; Fruergaard and Astrup, 2011); abatement of acidification phenomena because of its lower sulfur content in comparison to fossil fuels (Uson et al., 2013; Garg et al., 2007); contribution to resource efficiency (Hinkel et al., 2019) and cost reduction (Uson et al., 2013); and most importantly, the contribution to resource recovery from waste of poor quality that would otherwise be disposed in landfills (Iacovidou et al., 2017a). Despite the energy consumed during SRF production, combustion processes that use SRF have high efficiency leading to

a positive overall balance between the energy used to produce SRF and energy recovery from SRF (ERFO, 2019; Saveyn et al., 2016).

Yet, a basic prerequisite for the wider uptake of SRF in industrial applications is to have a predefined and most importantly stable SRF quality that is accurately and precisely determined; constituting a major technical challenge for SRF production plants (Flamme and Geiping, 2014). This challenge is attributed to the inherent heterogeneous composition of solid waste (Velis et al., 2010) arising from the wide variety of consumer products that become waste and the different seasonal and geographical consumer habits (Gajdoš Kljusuric et al., 2015; Beckmann et al., 2012; Liu et al., 2019).

The inherent heterogeneity of MSW and therefore SRF at multiple levels (assembly of items, components, materials, chemical compounds) is the main limiting factor for turning waste into secondary resources and therefore impedes the transition towards the circular economy (Esbensen and Velis, 2016; EERE, 2019). The inherent heterogeneity of SRF leads to an unpredictable thermal behaviour during co-combustion, creating challenges for operators to achieve optimum substitution rates (Beckmann et al., 2012). SRF quality depends on the feedstock/waste composition and the technology/processes used for the SRF production (Nasrullah et al., 2013; Nasrullah et al., 2015). Improving quality therefore may lead to higher cost (Sharabaroff et al., 2017).

SRF characterisation on the basis of a more complete list of its properties (**Section 2.1.**) is important for successful SRF marketability (Thomé-Kozmiensky, 2002). Among the properties, thermal behaviour (Hilber et al., 2007b) and chlorine (Cl) content (Pomberger and Sarc, 2014) are the most critical factors for end-users. Therefore it is important to understand: what tools can be used to reliably define the thermal behaviour of SRF before its utilisation (Hilber et al., 2007b)? Moreover, considerable amounts of Cl can be found in SRF due to the presence of chlorinated plastics and other materials (Chiemchaisri et al., 2010; Nasrullah et al., 2016). Chlorine is a critical technical parameter for SRF application because its presence can result in the formation of HCl – a caustic and highly corrosive chemical agent – during thermal processing (Ma et al., 2010). The need to discover the sources and variability of Cl in SRF during co-combustion is revealed.

SRF properties are determined by its physical composition (Hilber et al., 2007b) and therefore a detailed understanding of fuel composition improves the controllability and safe operation of co-combustion facilities (Hinkel et al., 2019). The importance of composition awareness to SRF QA has been stressed by researchers (Velis et al., 2010; Garg et al., 2007). SRF composition needs to be put into a process control system on continuous basis so that to adjust accordingly and maintain the desired fuel quality (Hinkel et al., 2019). If SRF composition is variable, operators must constantly adjust the flow and plant parameters to optimize their operations which can be complex, time-consuming and inconvenient. Therefore, the market values consistency and stability of chemical and physical parameters over an individual property (SUEZ, 2018).

For the production of a stable and assured fuel quality, establishing quality assurance (QA) measures is necessary to support SRF manufacturers in producing a fuel with consistently low variability and end-users to control actual performance in WtE processes (Velis et al., 2010; Flamme and Geiping, 2014). Inherent material heterogeneity can introduce significant uncertainty during laboratory sampling and sample preparation and therefore compromises the accuracy of analytical results (Edjabou et al., 2015; Nocerino et al., 2005). Thus, any individual set of values obtained from waste analysis may give invalid results and, therefore, misinformed conclusions (Wagner and Esbensen, 2015; Rupp and Jones, 1992; Gerlach and Nocerino, 2003). For example, a fragment of PVC contained in a particular SRF sample received for analysis could lead to the overestimation of Cl content (Flamme and Geiping, 2014).

In the content of other wastes, SRF could be considered to exhibit medium variability (Kallassy et al., 2008; Velis et al., 2010): not as low as industrial waste (e.g. plastic production scrap) or as the high as raw MSW variability, but certainly more homogenous as a consequence of the way it is mechanically processed (Velis et al., 2012; Chang et al., 1998). This makes it ideal for for advancing waste characterisation and waste-derived products techniques.

The following chapter of literature review of this Thesis (**Chapter 2**) serves three purposes. First, it provides a general description of SRF (**Section 2.1.**) focusing on its application in cement industry which is the main end-user (**Section 2.2**), and the current status of SRF QA (**Section 2.3**). Second, the

main QA limitations for a wider SRF uptake are presented (**Section 2.4**). The heterogeneous composition of SRF is discussed at multiple levels (waste categories, items, materials and chemical compounds) in **Section 2.4.1**, and the variable thermal behaviour and chlorine content in SRF are explained in **Section 2.4.2** and **Section 2.4.3**, respectively. Third, the importance of QA measures for SRF characterization creating and securing viable market outlets (**Section 2.5**) is discussed with a focus on laboratory sampling and sample preparation procedures (**Section 2.5.1**), analytical chemistry (**Section 2.5.2**), and choice of statistical tools (**Section 2.5.3**). **Chapter 2** led to the formation of research aim and objectives (**Chapter 3**).

2 LITERATURE REVIEW

2.1 Solid recovered fuel (SRF): description and properties

SRF is typically manufactured from high calorific fractions of non-hazardous solid waste and its composition meets national and EU specifications for co-combustion applications (Flamme and Geiping, 2012; Velis et al., 2010). Specifically, SRF is a WDF typically produced from individual or mixed streams of MSW, commercial and industrial waste (C&I), and construction and demolition waste (CDW), that meets the specification requirements laid down by a technical committee of European Committee of Standardization (CEN/TC 343) (BS EN 15359, 2011). SRF is produced in mechanical treatment (MT)/ mechanical biological treatment (MBT) plants which employ a series of processes including multistage shredding, sorting technology for separation of ferrous metals, inert materials, and other unwanted material such as polyvinyl chloride (PVC), and biodrying (Beckmann et al., 2012; Sarc et al., 2014). These waste treatment processes are widely applied in several countries having an influence on the residual waste stream for landfill disposal through sorting out waste materials that cannot easily be recycled for energy recovery (Martignon, 2020).

SRF can be used as an alternative co-fuel in the industrial sector mainly including cement industry – a primary SRF end-user – and coal-fired power plants, in WtE plants that are built exclusively to exploit the energy content of waste-derived materials, and in commercial facilities – quite limited so far – for thermochemical recycling (Martignon, 2020). SRF application in cement plants is more profitable than combustion in WtE plants due to lower investment cost and higher percentage of energy recovery (Theulen, 2015; Samolada and Zabaniotou, 2014).

The European Recovered Fuel Organisation (ERFO) data showed that the potential SRF production from MSW, C&I waste and CDW in Europe is approximately 17.5, 20 and 19 Mt per year, respectively, and the potential SRF use is around 50 Mt per year with cement industry using 12 Mt per year (Cuperus, 2019). However, the current use of SRF in Europe is 13.5 Mt with cement industry making up the 40% of this total (ERFO and Cembureau, 2015).

Another WDF with similar composition to this of SRF is the refuse derived fuel (RDF) which is also produced in MT/MBT plants. Notably, and leading to confusion, the terms SRF and RDF are often used interchangeably due to their similar composition (e.g. both being produced from MSW). RDF is

a WDF described by ASTM standards dating back in the 1980s in the US (Milne et al., 1990), often today combusted in dedicated WtE plants, for instance in fluidized bed reactors (Dalai et al., 2009). However, the recent de facto conventions on the different scope for the terms ‘SRF’ and ‘RDF’ should be clarified: the former defined as complying with the standards established by the CEN/TC 343 putting on place quality assurance (QA)/ quality control (QC) schemes, while the latter does not follow the CEN quality management procedures, or any at all and, therefore, its content and quality being more variable and not sufficiently specified by regulatory schemes (Velis et al., 2010). **Figure 2-1** provides the difference and the relationship among the terms SRF, RDF and WDF.

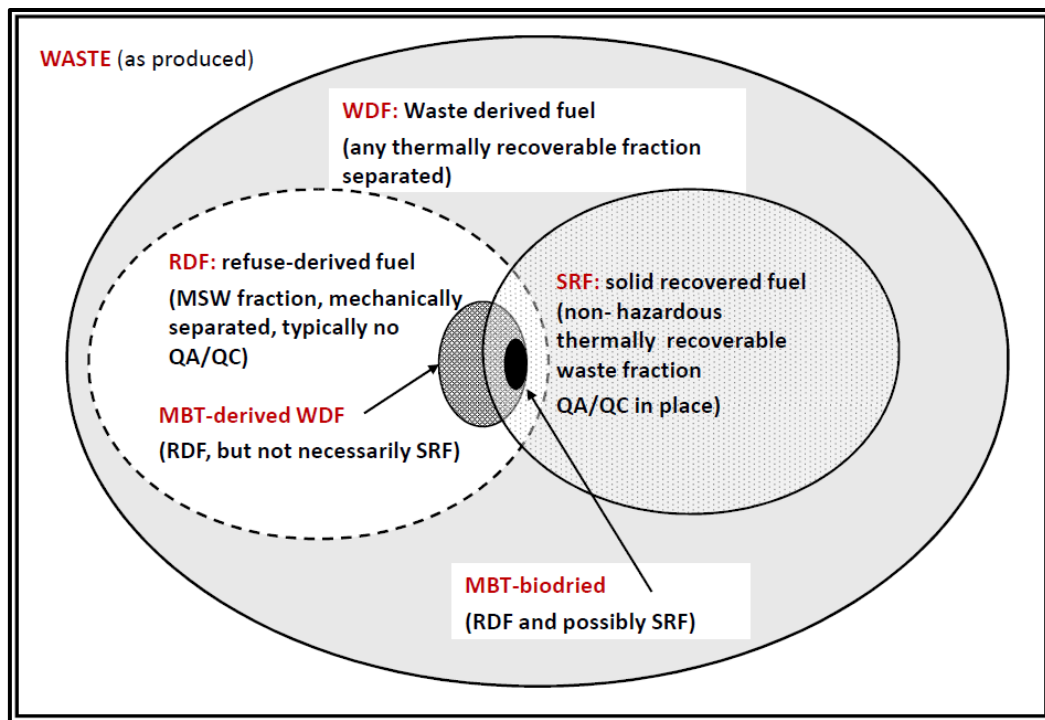


Figure 2-1. Terminology explanation for thermally recoverable waste fractions produced in MBT plants: WDF, SRF and RDF. Adopted by Velis et al. (2010).

The CEN technical standard laid down in the EN 15359 for SRF specification and classes constitutes a simplified and widely applied tool for SRF QA/QC in Europe (Velis et al., 2010). This classification scheme specifies SRF properties against three quality criteria: calorific value, the key economic attribute; Cl content, the key technical attribute; and mercury content, the key environmental performance attribute (BS EN 15359, 2011). More details are described in **Section 2.3**. However, the determination of a wider range of SRF properties is required to fulfil the requirements of end-users

(Beckmann and Thome-Kozmiensky, 2006). Velis et al. (2010) reported a completed list of properties for sufficient characterisation of WDF divided into four categories (Velis et al., 2010):

- Chemical properties including content of combustible and non-combustible matter, content of fixed carbon, content of volatile substances, concentration of trace elements (e.g. heavy metals), elemental composition (C, H, N, O), and content of major elements (e.g. chlorine and sulfur);
- Mechanical properties including particle size distribution, grindability, dispersability, density of combustible and non-combustible matter, particles properties (e.g. bulk density and shape), and shelf life;
- Calorific properties including lower- and upper- heating value, minimum air flow rate requirements, minimum flue gas temperature, adiabatic combustion temperature, thermal capacity, thermal conductivity, and temperature diffusivity;
- Reaction technical properties including thermal behaviour and corrosion potential.

2.2 SRF application in cement industry: a primary end-user

Cement manufacture is an intensive process with regards to fuel, electricity consumption and greenhouse gas (GHG) emissions (MPA Concrete Centre, 2017; Saveyn et al., 2016). Hence, the cement industry faces important challenges in meeting circular economy and decarbonisation goals, such as those set within the EU (Cembureau.eu, 2016; WSP and DNV GL, 2015). The European cement industry already meets a considerable part of its fuel demand with combustible waste. For example, in 2015, the cement industry in the UK replaced 42% of its thermal energy needs with WDF as an alternative to primary fossil fuels (MPA Concrete Centre, 2017). Use of WDF in cement kilns is favoured due to: i) operating conditions, such as alkaline environment, ash retention in the clinker (inorganic content is trapped and combined in the product (Chinyama, 2011)), good mixture of gases and products and high combustion temperature and flue gas residence time (Beckmann et al., 2012; Mokrzycki and Uliasz-Bocheńczyk, 2003); and ii) the experience of cement industry in handling a

range of WDF (Garg et al., 2009). In addition, cement kilns that adopted best available techniques (BAT) to comply with regulatory requirements do not require major alterations in the existing kiln system configuration (Schorcht et al., 2013; Hinkel et al., 2019).

SRF application in cement kilns and similar processes (e.g. lime kilns) can be regarded as an integrated part of modern waste management that substitutes fossil fuels and primary raw materials, improving resource efficiency (Hinkel et al., 2019). This option is considered a sustainable waste recovery option, offering cost savings means by avoiding consumption of primary fossil fuels, decarbonising the cement industry and preventing wider natural resources (Uson et al., 2013; Chatziaras et al., 2016; MPA Concrete Centre, 2017). Hinkel et al. (2019) stated that SRF co-processing in cement industry can give added value to waste systems operated by municipalities and improve waste management outcomes for stakeholders in industrial, commercial and agricultural sector. The European Commission policy recommendation on the use of WtE processes considers this option (SRF co-combustion in cement kilns) as one of the most energy efficient technology, to be prioritised as a WtE solution comparatively more compatible with a circular economy (European Commission, 2017). The current average efficiency of SRF co-combustion in cement kilns is ca 75%, defined as the heat recovered from waste input energy content (Saveyn et al., 2016).

Co-combustion of SRF in cement kilns is an established WtE process already widely adopted in Europe (ERFO and Cembureau, 2015; Theulen, 2015). The thermal substitution rate of traditional fossil fuels by SRF in an individual plant currently can range between 40% and 70% (Saveyn et al., 2016). For example, the Polish cement industry covered more than 50% of its fuel demand with SRF (ERFO, 2017); with the largest operator, HeidelbergCement, reaching a mass substitution rate of 70% in 2016 (ERFO, 2017). However, SRF utilization may affect the clinker manufacturing process and induce operating problems in the kiln, depending on the fuel quality. For example, SRF particles, which are larger than solid fossil fuels, can lower the gas temperature and degrade the cement quality, due to delayed ignition and slower thermal conversion, resulting in insufficient burnout and a large amount of particles falling onto the clinker bed (Liedmann et al., 2017).

The substitution rate of traditional fossil fuels by using SRF in cement kilns depends on the feeding point (primary firing, secondary firing), the conveying technology, plus the fuel composition and quality (Scur, 1998). During co-combustion in cement kilns, the ash of the fuel is incorporated into the clinker and therefore it can affect the quality of the product (Chinyama, 2011). There are a number of potential fuel feeding ports in a cement plant (Cement Sustainability Initiative, 2005; Sarc et al., 2014; Schorcht et al., 2013): i) via the main burner at the rotary kiln outlet end; ii) via secondary burners to the riser duct at the kiln inlet; iii) via precalciner burners to the precalciner; and iv) via feed chute to the precalciner (Schorcht et al., 2013). Feeding via the main burner requires relatively higher quality of SRF compared to other feeding ports (Sarc et al., 2014).

The market price of petcoke and the fees of alternative waste treatment options affect the financial attractiveness of SRF use in cement kilns (Hinkel et al., 2019). Different costs and revenues arise from SRF co-combustion depending on the waste management activities at municipal level: savings from sorting out of recyclables and substitution of fossil fuels, but there are costs related to collection, transportation, and operation of processes employed in MT/MBT plants for SRF production (WRAP, 2009; Hinkel et al., 2019). Therefore, SRF use can be financially attractive for cement off-takers (buyers under an offtake agreement), if the cost reduction from the substitution of fossil fuels leads to an increased competitiveness and the associated risks are reduced (Hinkel et al., 2019). This condition can be achieved by improving the quality of SRF, which is subject to technical and QA limitations, with Cl content being one of the most important (Cuperus, 2011; Lechtenberg and Diller, 2012). More details on the sources of Cl in SRF and the related implications in cement industries are described in **Section 2.4.3.**

2.3 Existing situation of SRF quality management in Europe

Quality management has a critical role in SRF marketability providing confidence in suppliers, end-users, and regulators (Velis et al., 2010), who otherwise feel uncomfortable about the application of WDF due to its unknown composition and therefore environmental and technical aspects (ERFO,

2019). The CEN/TC 343 initiative was established to develop relevant European standards for the market of SRF according to scientific research and extensive validation process through the QUOVADIS (QUality Management Organisation, VALidation of Standards, Developments and INquiries for Solid-Recovered Fuels) project. For the process of standardization, national standardization bodies, research institutes, industry and the European Environmental Citizens Organisation for Standardisation (ECOS) have participated (ERFO, 2020). Specifically, CEN/TC 343 elaborated European standards for SRF on the following issues (CEN/TC 343, 2018):

- Quality management systems to deliver wider confidence to SRF production and trading, determine the used documentation for internal procedures, communicate to related parties the specifications required to reach the quality objectives, and verify the origin and the properties of the input waste materials;
- Safety to define health risk associated to SRF production, handling, storage , trade, sampling and analysis;
- Specifications and classes forming the core of SRF standardization that specifies SRF properties against three quality criteria, following specific compliance statistics criteria for assessing the risk posed: net calorific value (NCV), the key economic attribute; Cl content, the key technical attribute; and mercury content, the key environmental performance attribute. Each parameter falls within five classes depending on the property value resulting in the assignment of SRF as a combination of three class number that defines its class code (**Table 2-1**). Notably, SRF classification and specification in not a single-time event, but the compliance to the limit values of each property is established under a 12 months period following a quality management system and sampling scheme;
- Determination of biomass content to define the contribution of SRF co-combustion to GHG emissions reduction including three analytical methods: selective dissolution method (SDM), manual sorting and ^{14}C method;

- Sampling and sampling preparation to assure the obtainment of reliable samples, which otherwise might lead to misleading SRF characterization due to its inherent heterogeneity, with respect to particle shape and size, and to composition;
- Chemical and physical analysis to describe proper methods for the determination of chemical and physical properties of SRF.

Velis et al. (2010) reported that CEN/TC 343 initiative aims to guarantee the fuel quality leading to the efficient trading of SRF by: providing access to permits for SRF use; enabling the rationalisation of design criteria for end-users; reducing the need for compliance monitoring; facilitating the communication with equipment manufacturers; and prescribing rules for SRF characterisations and classification (Velis et al., 2010). The class codes of the CEN/TC 343 classification scheme (**Table 2-1**) constitute a useful and immediate tool for quality identification and therefore SRF selection. However, it is a simplified assessment tool resulting inevitably in an inability to assess the actual performance of SRF during co-processing (Velis et al., 2010). In order the marketability of SRF be successful, the determination of a complete list of SRF properties and value ranges, thresholds and limits related to particular technical characteristics of each SRF application and legal demands relevant to thermal recovery processes are required (Velis et al., 2010). Other properties not included in the final classification scheme are used to define the quality of WDF with the most prevalent being the moisture content – an economic indicator (e.g. increased moisture decreases the heating value of the fuel), the ash content – a technical performance indicator (e.g. ash content can cause particulate emissions (Ma et al., 2010; Jin et al., 2016; Cortada Mut et al., 2015)), and the sum of potentially toxic elements (PTEs) – an environmental indicator (WRAP, 2012).

Table 2-1. Simplified quality characterisation ('Classification') of SRF according BS EN 15359 (2011), the core document of the most comprehensive set of standards available for SRF. The three SRF quality indicators measured by specific compliance statistics and sampling process.

Classification characteristic	Performance category	Statistical measure *	Unit	Classes				
				1	2	3	4	5
Net calorific value (NCV)	Economic	Arithmetic Mean	MJ kg ⁻¹ (ar)	≥ 25	≥ 20	≥ 15	≥ 10	≥ 3
Chlorine (Cl) [Total]	Technological	Arithmetic Mean	% (d)	≤ 0.2	≤ 0.6	≤ 1.0	≤ 1.5	≤ 3
Mercury (Hg)	Environmental	Median	mg MJ ⁻¹ (ar)	≤ 0.02	≤ 0.03	≤ 0.08	≤ 0.15	≤ 0.50
		80 th percentile	mg MJ ⁻¹ (ar)	≤ 0.04	≤ 0.06	≤ 0.16	≤ 0.30	≤ 1.00

* Quality control practices require statistical tools to ensure the consistency and compliance to current specifications of SRF properties, such as unbiased estimates for central tendency (arithmetic mean, median), spread of values (e.g. standard deviation, coefficient of variation), and upper/lower confidence limits. The properties of SRF need to be specified by a level of uncertainty (Velis et al., 2010).

Table 2-2 presents the existing standards established by CEN/TC 343 for QA/QC of SRF addressing all the related issues mentioned above. Despite CEN/TC 343 standards, a variety of national QA/QC initiatives for WDF have been also adopted in Europe. Velis et al. (2010) provided an overview of other national and trade QA/QC schemes for SRF adopted in Europe.

Table 2-2. CEN/TC 343 standards for QA/QC of SRF at different production stages implemented by the British Standard Institution.

Standard	Description	Focus area	Production stage	Publication type
(BS EN 15358, 2011)	QMS – Particular requirements for their application to the production of solid recovered fuels	QMS	Pre-production, production	BS EN*
(BS EN 15357, 2011)	Terminology, definitions and descriptions.	QMS	Pre-production, production	BS EN*
(BS EN 15359, 2011)	Specifications and classes.	Classification scheme	Pre-production, production	BS EN*
(BS EN 15442, 2011)	Methods for sampling in the production plants	Sampling and sample preparation	Production	BS EN*

(BS EN 15413, Methods for the preparation of the test 2011)	Sampling and sample from the laboratory sample.	Sampling and sample preparation	Post-production	BS EN*
(BS EN 15443, Methods for the preparation of the 2011)	laboratory sample.	Sampling and sample preparation	Production	BS EN*
(BS EN ISO 21912, 2011)	Safe handling and storage of solid recovered	Safety	Production,	DIS**
(BS EN 15590, 2011)	Determination of the current rate of aerobic microbial activity using the real dynamic respiration index.	Safety	Post-production	BS EN*
(BS EN 15407, 2011)	Solid recovered fuels. Methods for the determination of carbon (C), hydrogen (H) and nitrogen (N) content.	Chemical analysis	Post-production	BS EN*
(BS EN 15408, 2011)	Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content.	Chemical analysis	Post-production	BS EN*
(BS EN 15440, 2011)	Methods for the determination of biomass content.	Determination of biomass content	Post-production	BS EN*
(BS EN 15403, 2011)	Determination of ash content.	Chemical analysis	Post-production	BS EN*
(BS EN ISO 22167, 2011)	Determination of content of volatile matter.	Chemical analysis	Post-production	DIS**
(BS EN 15400, 2011)	Determination of calorific value.	Chemical analysis	Post-production	BS EN*
(BS EN 15414-3, 2011)	Determination of moisture content using the oven dry method.	Chemical analysis	Post-production	BS EN*
(BS EN 15411, 2011)	Methods for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn).	Chemical analysis	Post-production	BS EN*
(BS EN 15410, 2011)	Methods for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn).	Chemical analysis	Post-production	BS EN*
(BS EN 15415-1, 2011)	Determination of particle size distribution. Screen method for small dimension particles.	Physical analysis	Post-production	BS EN*
(BS EN 15415-2, 2011)	Determination of particle size distribution. Maximum projected length method (manual) for large dimension particles.	Physical analysis	Post-production	BS EN*

(BS EN 15415-3, 2011)	Determination of particle size distribution. Method by image analysis for large dimension particles.	Physical analysis	Post-production	BS EN*
(DD CEN/TS 15405, 2010)	Determination of density of pellets and briquettes.	Physical analysis	Post-production	DD***
(DD CEN/TS 15406, 2010)	Determination of bridging properties of bulk material.	Physical analysis	Post-production	DD***
(DD CEN/TS 15639, 2010)	Determination of mechanical durability of pellets.	Physical analysis	Post-production	DD***
(DD CEN/TS 15404, 2010)	Methods for the determination of ash melting behaviour by using characteristic temperatures.	Physical analysis	Post-production	DD***
(DD CEN/TS 15401, 2010)	Determination of bulk density.	Physical analysis	Post-production	DD***
(DD CEN/TS 15412, 2010)	Methods for the determination of metallic aluminium.	Physical analysis	Post-production	DD***

*British standard implementation of English language versions of European standards; ** Draft International Standard: enquiry draft of an ISO standard equivalent; ***Draft for development: under development, eventually be withdrawn and replaced

2.4 QA requirements of SRF end-users: critical aspects

The quality of SRF is mainly affected by three critical factors including the degree of variability, the level of desirable properties, and the concentration of contaminants (Velis et al., 2010). The variability of SRF quality due to the high inherent heterogeneous composition of feedstock (e.g. MSW) leads to inconvenience of SRF application by end-users and regulators (ERFO, 2020). Thus, the production and assurance of quality-certified SRF with acceptable levels of variability is critical for MT/MBT plants (Velis et al., 2010). SRF quality mainly depends on the effectiveness of mechanical processing configuration and quality of waste input (Di Lonardo et al., 2012).

2.4.1 SRF/RDF inherent heterogeneous composition

Despite the difference between SRF and RDF in terms of terminology, their similar composition (e.g. produced from MSW) served as the basis for the term SRF/RDF used at this section. SRF/RDF is a complex and inherent heterogeneous mixture of components at multiple levels including an assembly of waste items, materials and chemical compounds.

2.4.1.1 Prevalent waste components categories (items/materials)

In a weight-related descending order, the most prevalent waste items in commercial SRF/RDF produced from MSW are *paper/cardboard*, *plastics*, *textiles* and *wood* (**Table 2-3**). Specifically, **Table 2-3** presents the composition of SRF/RDF derived from MSW – the prevalent source of SRF production – on the basis of waste item/categories determined by recent studies conducted over the last 10 years (2009-2019). Older studies were not included in **Table 2-3** due to the dependence of MSW composition and therefore SRF/RDF on time leading to misinformed estimation of the current fuel composition (Brunner et al., 2004; Abdel-Shafy and Mansour, 2018; Pomberger et al., 2017). For example, the global production of plastics was increased by nearly 18% from 2010 to 2015 (Hannah and Max, 2019). More importantly, the reduction of landfill disposal rates (ca. 36% for the period 1995-2014) and the increased recycling and composition rates (27%) over the last decades due to legal requirements resulted in increased WtE rates (nearly 13%) in EU-28 (Pomberger et al., 2017). However, **Table 2-3** is in agreement with Vainikka et al. (2011), who collected literature findings from older studies to identify a typical SRF composition. Specifically, *paper/cardboard* fluctuated in a range of 40-50% w/w, *plastics* 25-35% w/w, *textiles* 10-14% w/w and *wood* 3-10% w/w. The comparison between the old ranges (from 2003 to 2009) reported by Vainikka et al. (2011) with the updated typical composition of SRF/RDF (between 2009 and 2019) in **Table 2-3**, indicate that SRF/RDF composition is more dependent on other factors rather than on time. Higher variability of SRF/RDF composition is observed among the recent studies of **Table 2-3** (over the last ten years) rather than between Vainikka et al. (2011) and **Table 2-3**. This might be attributed to the different quality of SRF samples depending on the type of waste input and multi-stage processing configurations (Sarc et al., 2019), seasonality (Beckmann et al., 2012) and geographical location (Kljusuric et al., 2015) and off-taker specifications (Sarc et al., 2019) and/or the potential bias in composition determination.

‘Fines’, consisting of several materials with particle size usually defined by the cumulative passing < 15 mm or less, constituting soil, dust, plastic fragments, glass, ferrous, organic, lithoid, ferrous and other fragments (Velis, 2010; Di Maria et al., 2013) can considerably affect the quality of SRF/RDF

(Nasrullah et al., 2016). Fines is typically an unwanted waste fraction because it reduces the calorific content of overall SRF/RDF due to its high content of non-combustible/inert materials; and because it concentrates contaminants such as PTEs (Nasrullah et al., 2014; Nasrullah et al., 2015). For example, Nasrullah et al. (2016) examined the mass flow of PTEs during SRF production in an MBT plant indicating a considerably higher proportion of mercury and arsenic of the input waste in the fine fraction compared to other output waste streams: 45% of total input was present in the fine fraction that was produced in primary shredding and screened out as reject fraction, 25% of total input was in other rejected fractions (heavy and polluted materials), whereas SRF contained only 30%.

Table 2-3 features data on the composition of SRF/RDF determined by both manual sorting and thermogravimetric analysis (TGA) – a thermal analytical technique widely applied for composition identification (Tessier, 2018). More details on the use of TGA for compositional analysis of SRF/RDF and determination of its thermal behaviour is described in **Section 2.4.2**. Comparison between the two techniques can be obtained only at the level of two main waste fractions of SRF/RDF – biomass and plastic content – since TGA results described the composition based on just these two fractions due to overlapping thermal degradation areas among waste items/materials (discussed onwards). By comparing the composition of SRF/RDF conducted through TGA with this of manual sorting at the level of biomass-based and plastic-based content, the two techniques (TGA and manual sorting) demonstrate similar SRF/RDF composition (**Table 2-3**).

Table 2-3. Typical composition of commercially produced SRF/RDF samples from MSW, based on most prevalent waste item categories over the last 10 years (from 2009 to 2019), expressed in as received reporting basis.

Paper/ cardboard (% w/w)	Plastics (% w/w)	Textiles (% w/w)	Wood (% w/w)	Fines (% w/w)	Other (% w/w)	Geographical location	References
30	33	10	8	13	6	Finland	(Nasrullah et al., 2016)
82	13	5 ^a				UK	(Wagland et al., 2011)
19	45	13	23 ^b			Latvia	(Porshnov et al., 2018)
47	31	7	4	1	10	UK	(Velis, 2010)
11	30	8	11	40 ^c		Poland	(Stępień et al., 2019)

59-65 ^d	28-31 ^d					UK	(WRAP, 2009)
10-40	10-40	0-20	0-20	2-7	2-40	UK	(DEFRA, 2014)
13 ^e	28 ^e	10 ^e	0-3	45 ^{e*}	1-4 ^e	Austria	(Sarc et al., 2014)
11	20	9	0-1	51 [*]	8-9	Austria	(Sarc et al., 2019)
30	28	14	0-10	5	13-23	Italy	(Di Maria et al., 2013)
56 ^f	27 ^f				17	USA	(Robinson et al., 2016)
79 ^f	21 ^f					UK	(Efika et al., 2015)
46-82 ^f	18-54 ^f					Greece	(Skodras et al., 2009)

^a 5% included wood, textiles and miscellaneous combustibles; ^b Defined as unidentified materials (composition derived from three different RDF samples); ^c The highest proportion of the fuel was unidentified and mineral waste (31.6% w/w_{ar}); ^d Defined as the residual stream after material recovery for recycling; ^e Values derived from two different SRF qualities, intended for main burner fuel and hot-disc fuel; ^{*} Fines defined by the cumulative passing < 11.2 mm; ^f Defined as cellulosic and plastic fraction using TGA

However, many waste products consist of a variety of components with different properties. For example, beverage cartoons consists of paper (ca. 75% w/w), aluminum (ca. 5% w/w) and low density polyethylene (LDPE) (ca. 20%) (Korkmaz et al., 2009). Each waste component category at item level, such as *textiles*, *wood*, *paper* or *plastics* accommodates for a tremendous variability at material or chemical compound level indicating that they are arbitrarily and loosely defined. In *textiles*, natural materials, such as cotton, wool and silk fibers, or synthetic materials, such as polyester, polyamide (PA) and acrylic fibers, or a combination of them under different proportions are used for the production of textile products (Pohl, 2010). Natural fibers are mainly composed of cellulose, which is a natural biomass polymer, whereas synthetic fibers are manufactured from mainly fossil-based polymers (Miranda et al., 2007). The different chemical composition between natural and synthetic fibers results in a wide range of properties and thermal behaviour of *textiles* at item level (Pohl, 2010; Miranda et al., 2007). Similarly, in the waste item category of *paper/cardboard*, raw materials used for papermaking can be divided into two categories: wood materials, such as softwood and hardwood fibers; and non-wood materials, such as grasses, cereal straws, corn stalks, bamboo, and bagasse (Liu et al., 2018). The fiber type and pulping process (e.g. chemical or mechanical) can lead to considerably different paper properties (Liu et al., 2018; Hubbe et al., 2007). In several species of solar biomass, the percentage participation of cellulose, hemicellulose and lignin varies considerably.

In general, hardwood and softwood have similar thermal behaviour, with the difference being that softwood has higher fire retardancy due to higher char formation (Wong et al., 2014). Pine and poplar wood are, respectively, representative of softwood and hardwood, found in MSW as, e.g., fruit boxes and plywood (Cozzani et al., 1995).

2.4.1.2 Prevalent polymers

The identification of polymer composition can give a deeper understanding of SRF/RDF thermal behaviour compared to that of waste items, which features higher variability. The identification of polymer composition can provide also valuable information on the quality of SRF/RDF such as its heating value, an economic attribute of the fuel (WRAP, 2009). For example, high content of lignocellulosic material tend to lower the heating value of the WDF, because of higher heating value (HHV) range at 12-21 MJ kg⁻¹ (Boumanchar et al., 2017; Zhao et al., 2016), whereas fossil-based plastics with HHV at 20-47 MJ kg⁻¹ increases their average heating value (Tsiamis and Castaldi, 2016).

Even within the same polymer type, considerable differences can be observed related to its macromolecular structure, which can affect the thermal stability of the polymer (Ray and Cooney, 2018). Specifically, all of: type and concentration of functional groups, polymer size as defined by the degree of polymerization and molecular weight (Francuskiewicz, 1994), degree of branching, cross-linking, crystallinity and amorphousness have impact on the thermal behaviour of a polymer (Ray and Cooney, 2018). For example, a branched polymer presents lower thermal stability compared to a polymer with linear structure, whereas the presence of hydrogen bonding enhances the thermal stability of polymers. In addition, cross-linked polymers, such as polyethylene (PE), have higher resistance to thermal degradation. Crystalline structures have higher stability than amorphous areas, whereas the higher the polymer size the higher the resistance to thermal degradation (Ray and Cooney, 2018). SRF/RDF is mainly composed of two fractions including a wide variety of polymer molecules: biomass (biogenic, i.e. of plant or animal origin) and fossil-based plastic.

a) Biopolymers content analysis of SRF/RDF

Biomass mainly features three biopolymers: cellulose, hemicellulose and lignin (Pérez et al., 2002), although other materials such as extractives, ash and trace elements are also present (Dufresne, 2012). SRF/RDF contains significant amounts of these polymers. Conesa and Rey (2015) determined the biomass content in three MSW-derived commercially produced SRF samples at 86.5% w/w, of which 61.1% w/w was cellulose, 31.3% w/w lignin, and 7.6% w/w hemicellulose.

Cellulose is widely used in papermaking, building, pharmaceutical, food and textile industries (Shokri and Adibkia, 2013; Lavanya et al., 2011; Osorno and Castro, 2018). Cellulose is a linear polysaccharide composed of glucose monosaccharide units. Each of its monomers bears three hydroxyl groups, which are involved in several hydrogen bonds either within the chain (intramolecular) or with other molecules (intermolecular) resulting in different crystalline arrangements (Dufresne, 2012; Park et al., 2010). The degree of crystallinity, the size and the orientation of the molecular chain determine the structure of the polymer. There are four different types of cellulose according to its crystalline structure: cellulose I, present in the majority of lignocellulosic plants, also known as natural; and the regenerated types of cellulose II, cellulose III and cellulose IV – as detailed further elsewhere (Nunes, 2017; Roy Choudhury, 2017; Park et al., 2010). The degree of crystallinity of cellulose is variable depending on the type of fibre. For example, cellulose from cotton has 70% degree of crystallinity (Wood, 1988), whereas in wood and plant fibres the degree of crystallinity ranges between 55-70% and 60-70%, respectively (Petroudy, 2017). In addition, degree of polymerization of cellulose widely varies between 1000 and 27000 (Hallac and Ragauskas, 2011; Dufresne, 2012). For example, the degree of polymerization in wood fluctuates nearly by 10000, whereas in cotton is ca. 15000 (Zhang and Lynd, 2004). Cellulose microfibrils that form the cellulosic fiber have variable orientation and length depending on the source (Dufresne, 2012; Béguin and Aubert, 1994). A seminal study stated that the degree of crystallinity, the degree of polymerization and the chain orientation considerably influence the thermal behaviour of cellulose (Basch and Lewin, 1973).

Hemicellulose is a biopolymer with several industrial applications, such as hydrogels, paper coatings and adhesives (Farhat et al., 2017). Its derivatives are also used in the food and pharmaceutical industry (Menon et al., 2010). Unlike cellulose, hemicellulose is a heterogeneous polysaccharide that

may be composed of several sugar units, such as galactose, glucose, mannose, xylose and arabinose (Pérez et al., 2002; McKendry, 2002). Hemicellulose is a branched polymer and the degree of polymerization can range between 80 and 200 (Gatenholm and Tenkanen, 2003; Spiridon and Popa, 2008). There are four main types of hemicellulose: xylans, mannans, xyloglucan and β -glucans with mixed linkages (Heinze and Liebert, 2012; Gatenholm and Tenkanen, 2003).

Specifically, xylan is the most abundant hemicellulose type that composes 20-30% of biomass plants (Heinze and Liebert, 2012; Pauly et al., 2013). Xylans consist of a linear β -(1,4)-linked xylose backbone, which can be substituted with acids or other substituents depending on the plant source (Pauly et al., 2013). A common type of substitution occurs where the xylose backbone is substituted with α -(1,2)-linked glucuronosyl and 4-O-methyl glucuronosyl residues, known as glucuronoxylans (Scheller and Ulvskov, 2010). The absence of a repeated structure results in many variations, not all well studied (Heinze and Liebert, 2012). In many studies, xylan was selected as a representative substance of hemicellulose in waste-derived materials (Heikkinen et al., 2004; Pérez et al., 2002; Raveendran et al., 1996; Yang et al., 2006; Cozzani et al., 1997). However, Cozzani et al. (1997) reported that the selection of xylans to represent hemicellulose could be misleading: it should be considered only as one of the common types of hemicellulose. Mannans are mainly used in the food industry and can be found in the wall of algae and gymnosperms (Pauly et al., 2013). There are different types of mannans, such as linear mannan, glucomannan, galactomannan and galactoglucomannan, depending on backbone composition and sidechain substitution (Scheller and Ulvskov, 2010). The prevalent type of hemicellulose in hardwood is glucuronoxylan (ca. 80-90% of total hemicellulose content), whereas in softwood is glucomannan (ca. 60-75% of total hemicellulose content) (Pérez et al., 2002; Spiridon and Popa, 2008; Grønli et al., 2002).

Lignin is the second most abundant plant polymer with wide application in several industries, such as building (e.g. dyes, paints and flooring), food, pharmaceutical, cosmetics, textile (e.g. fire retardant coating on textiles) and heat and power plants (Mandlekar et al., 2018; Watkins et al., 2015; Berlin and Balakshin, 2014). Lignin is the most heterogeneous biopolymer due to its variable structure regarding polymer size, composition, cross linking and functional groups (Dence and Lin, 1992). This variability affects its reactivity and thus, its thermal behaviour (Ibrahim et al., 2011). The composition

of lignin differs not only between plant species, but also between parts of the same plant (Gosselink et al., 2004). Lignin is an amorphous polyphenolic polymer with high molecular weight that mainly consists of three phenylpropanoid units: i) trans-pcoumaryl alcohol (H unit); ii) trans-coniferyl alcohol (G unit); and iii) trans-sinapyl alcohol (S unit) depending on the plant species (Ibrahim et al., 2011). Lignin in softwoods mainly consists of G units, while in hardwood it is composed of G and S units, in a ratio ranging from 4:1 to 1:2 (Wikberg, 2005). These monomeric units form a randomized structure in a three-dimensional network inside the cell wall yielding a vast number of functional groups and linkages: i) structure I that can be found in plants, such as grass; ii) structure II in the wood of conifer plants; and iii) structure III in the wood of deciduous plants (Ibrahim et al., 2011; Gellerstedt and Henriksson, 2008; McKendry, 2002; Watkins et al., 2015). Different functional groups, such as hydroxyl, methoxyl, carbonyl and carboxylic, can be found in lignin at different proportions (El Mansouri and Salvadó, 2007). It is difficult to measure the degree of polymerization of lignin due to the polymer fragmentation during extraction (Polymer Database, 2019a).

In addition to the native lignin in its original form, technical lignin is produced as a byproduct from pulping or cellulosic ethanol processes (Li and Takkellapati, 2018). Gani and Naruse (2007) reported a morphological difference between technical and native lignin that can affect its thermal behaviour. The chemical composition of technical lignin may vary considerably depending on the type of raw material, delignification process and pulping conditions (Polymer Database, 2019a; Sameni et al., 2014). The main technical lignins are kraft, sulfite and soda lignin extracted through kraft, sulphite and soda pulping, respectively (Lu et al., 2017). The first two pulping processes accounting for more than 90% of the chemical pulp production worldwide (Ahvazi et al., 2016).

b) Fossil-based plastics content analysis of SRF/RDF

Unlike biomass polymers, there is a wide variety of fossil-based plastic polymers in MSW with the most prevalent being PE, polypropylene (PP), PVC and polyethylene terephthalate (PET) due to their predominance in plastic packaging, which accounts for 40-60% of overall plastics waste generation (European Commission, 2018; Bodzay and Bánhegyi, 2016). Only polyolefins (PE and PP) accounted

for ca. 60% of overall plastics production in EU-28 (Villanueva and Eder, 2014; PlasticsEurope, 2019a).

Polyethylene can be categorised based on its density, with the most common types being LDPE and HDPE. Both PE types have similar properties, although HDPE has higher tensile strength. HDPE is mainly used for the production of bottles, packaging products with short shelf life and packaging of chemicals due to its high stiffness, barrier properties and chemical resistance, respectively (Villanueva and Eder, 2014). LDPE is mainly used for the production of plastic films due to its toughness, transparency and flexibility (PlasticsEurope, 2019b).

The second most prevalent plastic polymer, PP, is found in two forms based on its stereochemical arrangement: isotactic PP characterized by high rigidity and hardness; and atactic PP, which is amorphous with less strength (Nicholson, 2017). However, the vast majority of commercial PP is isotactic (90-95%) (Nicholson, 2017), found in flexible and rigid packaging products (Villanueva and Eder, 2014). Similarly to PE, isotactic PP has high tensile strength and chemical resistance (Maddah, 2016; Polymer Database, 2019b; Gabbott, 2008).

The presence of textiles and beverage bottles are the reasons that PET is one of the prevalent fossil-based polymers in SRF/RDF (toughness, high resistance to most solvents and clear and optically smooth surfaces (Villanueva and Eder, 2014)): not all of them are collected for recycling and therefore, may de facto and for now still constitute part of SRF/RDF. Specifically, polyester fibers from PET constitute the most widely used synthetic fiber in the textile industry (Ravindranath and Mashelkar, 1984; Van der Velden et al., 2014; Sarioğlu and Kaynak, 2017). In 2015, nearly 15% of global plastic production is used in textile industries for the production of synthetic textiles (Geyer et al., 2017). PET accounts for 70% of global production of polyester, polyamide and acrylic fibers (Geyer et al., 2017).

PVC is used in a variety of applications, such as construction, building, automobile and packaging industries due to its excellent processing performance, resistance to oil and chemical reaction and high strength (Villanueva and Eder, 2014). However, PVC is an unwanted component in SRF/RDF due to

its high chlorine (Cl) content (46-54% w/w (Phyllis, 2019)). Although, NIR technology is an applied sorting process in MBT plants for the removal of PVC, still PVC fragments are present in SRF/RDF.

2.4.1.3 Composition of synthetic SRF/RDF samples

A method to obtain insights into the thermal behaviour of SRF/RDF is to artificially prepare synthetic mixtures with a known composition similar to SRF/RDF. This approach is undertaken due to the difficulty in conducting compositional analysis in commercially manufactured samples. **Table 2-4** presents several examples of synthetic SRF/RDF samples as prepared in previous studies. The biomass fraction of simulated SRF/RDF is mainly composed of *paper* and/or *wood*. However, the composition of plastic fraction is more complicated due to the wide variety of post-consumer plastic polymers. According to Grammelis et al. (2009), cardboard and magazine paper can represent the biomass fraction of SRF/RDF better than other biomass waste items, whereas PE resembles more closely the plastic fraction compared to other plastics. The main reason that synthetic SRF/RDF samples contain PVC, which is the exclusive or the prevalent source of Cl, is that Cl should be present in order to resemble the genuine SRF/RDF.

However, significant inconsistencies can be noticed between the thermal behaviour of synthetic and genuine waste samples with similar composition due to the presence of plastic additives or other unknown substances in the genuine sample (Grammelis et al., 2009; Cuperus et al., 2005). For example, heat stabilizers are widely used in food plastic packaging to prevent polymer decomposition when exposed at elevated temperatures resulting in higher thermal stability compared to their synthetic pure counterparts (Hahladakis et al., 2018).

Table 2-4. Composition of synthetic SRF/RDF samples prepared to simulate the actual composition of SRF/RDF as received reporting basis.

	Paper	Plastics	Textiles	Wood	Other	References
Biomass	58		15	5 ^a		(Wagland et al., 2011)
Plastics	PE	12				
	PP	8				
	PVC	2				

Biomass		46.1	3.1 ^b	2.3 ^c	8.5 ^d	(Cuperus et al., 2005)
Plastics	PE	23				
	PP	16				
	PVC	1				
Biomass				50 ^e		(Pedersen et al., 2016)
Plastics	PE	50				
	PP					
	PET					
Biomass				44-62		(Chiemchaisri et al., 2010)
Plastics		38-56				
Biomass		46				(Wang et al., 2002)
Plastics	PE	50.4				
	PVC	3.6				

^a Conifer saw dust; ^b Sackcloth; ^c Pallet; ^d Grass; ^e Pine wood

2.4.2 Assessment of SRF thermal behaviour

A straight definition of the thermal behaviour of SRF cannot be obtained due to its constitutional heterogeneity (Hilber et al., 2007b). However, thermal analysis could give insights into the thermal behaviour of SRF/RDF and therefore prevent risks, optimize combustion performance, leading to confidence on SRF/RDF uptake in co-combustion/ dedicated WtE outlets. The thermal degradation of SRF/RDF is mainly a result of the thermal degradation of the biogenic (cellulosic) and plastic fraction (Danas and Liodakis, 2018). SRF/RDF is decomposed in a wider temperature range at lower levels compared to fossil fuels due to its low fixed-carbon and high volatile matter (Akdağ et al., 2016; Skodras et al., 2009). For example, the range of decomposition temperature of coal is 700-800 °C and petroleum coke is 500-700 °C, whereas for SRF/RDF this range is 200-600 °C (under combustion) (Akdağ et al., 2016). However, SRF/RDF has higher thermal resistance than MSW (Azam et al., 2019). Azam et al. (2019) reported that the peak decomposition temperature of MSW was lower (295 °C) than this of RDF (341 °C), whereas the range of decomposition temperature was wider for MSW (220-560 °C) compared to RDF (236-554 °C).

A wide variety of thermal analytical techniques are available to measure a thermal property of SRF/RDF sample, following a predetermined heating profile (Cheremisinoff, 1996). TGA is one of the most widespread thermal analytical techniques, considered to be rapid, accurate, affordable and user-friendly (Gomes et al., 2018; Ray and Cooney, 2018; Beyler and Hirschler, 2002). More information on thermal analysis and its application areas are reported by Gabbott (2008).

2.4.2.1 Thermogravimetry (TGA): a promising tool

TGA measures the mass change of a substance as a function of temperature or time due to decomposition, oxidation and loss of volatiles under a specified temperature programme and atmospheric conditions (Heal, 2002; Garcia et al., 2013; Ramalingam and Ramakrishna, 2017; Murty et al., 1996). TGA can be performed either by gradually raising the temperature of the sample under a constant heating rate (*non-isothermal* conditions), or by keeping a constant temperature and recording the mass loss as a function of time at a fixed temperature (*isothermal* conditions) (Vyazovkin and Wight, 1997; Heal, 2002). The practical problem with the selection of *isothermal* conditions is the partial degradation of the sample before the desired temperature is reached, losing significant thermal information (Beyler and Hirschler, 2002).

TGA is often combined with derivative thermogravimetry (DTG) performing the rate of mass loss (Heal, 2002). Three characteristic temperatures indicating the reactivity of a sample and its conversion behaviour can be obtained from the TG-DTG thermogram: (i) onset temperature (T_o), at which fuel starts to thermally degrade (drying and partial volatilization); (ii) DTG peak temperature (T_p), at which the rate of mass loss is maximum (decomposition) (Bottom, 2008); and (iii) endset temperature (T_e), at which the rate of mass loss decreases to $1\% \text{ w/w min}^{-1}$ (He et al., 2013; Hilber et al., 2007b). TG-DTG curves provide both qualitative and quantitative information: qualitative includes identification of substances; and quantitative includes percentages of mass loss and characteristic temperatures at critical points (Xu et al., 2005). In waste materials, DTG thermogram consists of a curve with several peaks/shoulders that correspond to a specific waste fraction that contains materials with similar devolatilisation behaviour (Piao et al., 2000). TG-DTG is used for compositional analysis and determination of reaction kinetics giving information on thermal stability, decomposition profile

and moisture, inorganic and volatile content of the sample (Murty et al., 1996; Ramalingam and Ramakrishna, 2017; Tessier, 2018). The simultaneous application of TG-DTG with other thermal analytical techniques, known as simultaneous thermal analysis (STA), that can detect physical changes (e.g. glass transition/melting point) is widely used to obtain additional information (Heal, 2002).

For compositional analysis purposes, the main disadvantage of TG-DTG especially for heterogeneous fuel mixtures is that the DTG curves of individual components in the mixture cannot be distinguished due to overlapping reactions at similar ranges of decomposition temperature (Heal, 2002; Piao et al., 2000). For that reason, TG-DTG is often combined with evolved gas analysis (EGA), such as Fourier transform infrared spectroscopy (FTIR), mass spectrometry (MS) and gas chromatography (GC), which determine the composition of the gas mixture evolved from the heated sample (Warrington, 2002). Several studies combined TG-DTG with EGA for the determination of thermal stability of SRF/RDF and MSW (Singh et al., 2012; Efika et al., 2015; Casu et al., 2006; Ma et al., 2019; Cheng et al., 2007; Edo et al., 2016a; Zhou et al., 2015; Chhabra et al., 2019; Fernández et al., 2012).

For TGA-based compositional analysis of complex and inherent heterogeneous waste-derived materials, the investigation of TG-DTG thermogram of the sample as a mixture of components can offer valuable insights. However, it should be noted that the identification of prevalent components and the determination of their thermal behaviour individually is not a sufficient approach on its own (Hilber et al., 2007b). SRF is a mixture of a huge variety of components, many of them hard to identify (e.g. the considerable fraction of 'fines') (Hilber et al., 2007b).

TG-DTG can be used as a tool to predict the composition of a complex mixtures by identifying individually TG-DTG profiles of the components of the mixture using statistical analysis. However, the selection of the level (item, materials or chemical compounds) at which the waste sample can be sufficiently described as a mixture of several components makes the use of TG-DTG for compositional analysis of WDFs quite challenging. This difficulty has led to another research direction, the description of thermal behaviour of SRF/RDF performing kinetic analysis with the use of TG-DTG (Bosmans et al., 2014; Grammelis et al., 2009; Azam et al., 2019), often combined with

EGA (Conesa and Rey, 2015; Singh et al., 2012). However, kinetics models are affected by the sample composition and experimental TG-DTG conditions which are both variable (Conesa and Rey, 2015) and therefore they might not be able to describe simultaneous reactions during the decomposition process (Masnadi et al., 2014).

Current research trends in solid waste management have shown that machine learning (ML), application of artificial intelligence aiming to automate analytical model building (Pezzè and Zhang, 2014), has been increasingly used for waste modelling. Specifically, ML algorithms, such as artificial neural network, support vector machine and regression and decision trees, were developed to build models for the prediction of the thermal behaviour of solid waste (Pandey et al., 2016; Çepelioğullar et al., 2016), the prediction of regional waste generation (Soni et al., 2019; Abbasi and El Hanandeh, 2016; Kontokosta et al., 2018; Kannangara et al., 2018; Johnson et al., 2017) and the prognostication of solid waste properties such as HHV (Rostami and Baghban, 2018).

A novel approach consisting of advanced thermal analytical techniques (e.g. TGA-EGA), statistically designed experiments (Design of experiments: DoE) able to simulate the composition and thermal behaviour of SRF/RDF (e.g. mixture design (Cornell, 2011)) followed by ML modelling could create robust tools (Salmaso et al., 2019) of QA/QC for finely shredded (fluff/pellet) SRF/RDF (e.g. <40 mm) that is hard/ impossible to identify otherwise (e.g. by manual sorting or TG-DTG on its own).

2.4.2.2 Thermal behaviour of SRF/RDF

Table 2-5 illustrates the main characteristic points of TG-DTG curves arising from the thermal behaviour reported for SRF/RDF. Differences among the decomposition profiles of SRF/RDF could be due to differing experimental conditions and differing composition of SRF/RDF samples between studies, e.g. the presence of food waste into SRF can lower its onset temperature (Edo et al., 2016a). It is worth mentioning that most researchers that used TGA for thermal analysis of WDF determined arbitrarily the temperatures at which the sample decomposition begins and completes, without referring to any definition. Therefore, the related temperatures presented in **Table 2-5** might be slightly different from the actual T_o and T_e temperatures. The maximum rate of mass loss obtained from the DTG curve in **Table 2-5** was not considered, because of inconsistencies in the relevant units,

and often missing information (e.g. sample mass) for the conversion unit. These observations reveal that the use of TGA as a tool for thermal and compositional analysis of SRF is a neglected side. Despite the great potential of TG-DTG, the importance of TG-DTG for assuring quality of SRF, is far from standardised or sufficiently developed in that capacity.

Table 2-5 shows that SRF/RDF is mainly decomposed in a range of 200-600 °C and its non-volatile content fluctuates between 10 and 20%. The DTG thermogram of SRF/RDF mainly consists of either two or three peaks/shoulders excluding the initial peak due to moisture evaporation. The first DTG peak represents the degradation of cellulosic fraction (200-400 °C) and the second represents the degradation of plastics (400-600 °C) (Efika et al., 2015; Edo et al., 2016a; Grammelis et al., 2009). The thermal decomposition of plastics at higher temperatures compared to lignocellulosic materials reveals the higher thermal stability of the plastic fraction (Skodras et al., 2009). The highest rate of mass loss was observed either in the first or in the second DTG peak depending on the composition of SRF/RDF. A last DTG shoulder might occur at elevated temperatures (600-700 °C) due to the interaction of char with gas (e.g. oxygen) along with ash deformation leading to the formation of mineral matter (Çepelioğullar et al., 2016). Grammelis et al. (2009) stated that the decomposition behaviour of SRF/RDF is comparable with that of beverage cartons, which was decomposed into two stages due to degradation of paper (200-400 °C) and plastic content (450-550 °C), respectively. Older studies conducted before 2009 found similar results with the current studies, although the waste composition changes over time due to the development of the MSW treatment performance, such as increasing recycling and composting rates (Pomberger et al., 2017). For example, Lin et al. (1999) reported two main distinct stages of mass loss during RDF pyrolysis (thermal treatment under inert atmosphere, e.g. nitrogen): the first stage due to cellulosic degradation and partial degradation of PVC (T_p : 327 °C) and the second due to plastics (T_p : 460 °C). Similar thermal profiles of RDF decomposition were found by Cozzani et al. (1995). There are also older studies that reported three DTG peaks at similar temperature ranges with those of recent studies (Cheng et al., 2007; Casu et al., 2006).

Table 2-5. Characteristic points of TG-DTG curves of SRF/RDF from MSW including onset temperature (T_o), endset temperature (T_e), number of DTG peak/shoulder, DTG peak temperature (T_p), and residue under specific experimental conditions (gas atmosphere and heating rate) over the last ten years as received reporting basis.

Atmosp. ¹	Heat. rate (°C min ⁻¹)	Decomposition temp (°C)		No. of peak	T_p (°C) ⁴	Residue (% w/w) ⁵	Ref.
		T_o ²	T_e ³				
Inert	10	200	800	2	312, 495	13	(Efika et al., 2015)
Inert	10	180	750	3	270, 470, 660	n.a	(Stępień et al., 2019)
Inert	10	n.a	n.a	2 ^a	336, 476	20	(Edo et al., 2016a)
Inert	10	200	500	2	310, 450	25	(Silva et al., 2015)
Inert	10	250	500	3	285, 352, 450	15	(Bosmans et al., 2014)
Inert	20	250	550	2	348, 480	20	(Grammelis et al., 2009)
Inert	20	200	550	2	350, 500	22	(Skodras et al., 2009)
Inert	20	230	700	n.a	320-340	12	(Tokmurzin et al., 2019)
Inert	25	180	700	3	342, 472, 670	17	(Robinson et al., 2016)
Inert	25	200	500	2	300, 470	n.a	(Singh et al., 2012)
Inert	5-50 ^b	200	750	3	325-365, 440-495, 645-710	20-24	(Çepelioğullar et al., 2016)
Oxidative	5	235		2-3 ^c	280, 440	n.a	(Medic-Pejic et al., 2016)
Oxidative	10	236	554	2	341, 465	9	(Azam et al., 2019)
Oxidative	10	200	540	2	340, 460	n.a	(Chae et al., 2019)
Oxidative	10	200	600	2 ^d	320, 500	21	(Akdağ et al., 2016)
				3 ^d	330, 400, 510	19	
Oxidative	10	200	500	3 ^a	225, 331, 461	n.a	(Edo et al., 2016a)
Oxidative	10	233	700	3	283, 463, 618	n.a	(Chen et al., 2018)
Oxidative	20	200	500	2	310, 460	11	(Grammelis et al., 2009)

¹ Atmospheric conditions: gas used in the TGA experiment; ² Onset temperature; ³ Endset temperature; ⁴ Peak temperature at each DTG shoulder; ⁵ Residue: non-volatile matter left after degradation; ^a Data derived from 3 samples that resemble RDF: one from residue of MSW containing plastics, paper, textiles and low amounts of food waste, and the other two from derived-materials consisting of residual MSW after drying and separation of incombustibles and food waste; ^b Eight different heating rates were used: 5, 10, 15, 20, 25, 30, 40, 50; ^c Derived from 10 different samples at different seasons and different locations; ^d Two different samples from two different cities; n.a: not available

a) *Thermal behaviour of prevalent waste component categories (item/material) in SRF/RDF*

Table 2-6 illustrates characteristic points of the TG-DTG curves of prevalent waste items/materials present in SRF/RDF categorised by the main waste items wood, paper and textile materials. The waste category of plastics is not provided in **Table 2-6** due to the preference of most researchers to investigate the thermal behaviour of plastic polymers as an alternative to post-consumer plastic materials (more details for the category of plastics is presented onwards). The degradation of the major biomass material occurs between 200 and 400 °C with a DTG peak temperature ranging from 355 to 370 °C (Sørum et al., 2001; Chen et al., 2015b; Cozzani et al., 1997). The decomposition of lignocellulosic components usually consists of two stages (DTG peaks): the first stage is attributed to the degradation of hemicellulose (200-350 °C), cellulose (250-400 °C) and partial decomposition of lignin (200-400 °C); and the second stage is attributed to the degradation of remaining lignin and charring of leftover (400-800 °C) (Skreiberg et al., 2011; Boumanchar et al., 2017; Porshnov et al., 2018; Heikkinen et al., 2004; Chhabra et al., 2019). In biomass mixtures, the DTG shoulder of hemicellulose might seem as a pronounced shoulder of cellulose rather than as a first well-defined DTG peak due to their similar decomposition ranges resulting in partial overlap (Grønli et al., 2002; Bosmans et al., 2014).

Table 2-6 shows that the DTG thermogram of *wood* contains either one or two DTG shoulders. This difference can be attributed to the incomplete degradation of lignin when the TGA experiment might be completed before the complete lignin degradation (around 900 °C) or to overlapping effects between cellulose and hemicellulose intensified by high heating rates. Slight differences might be observed between the TG-DTG thermograms of softwood and hardwood due to different chemical composition. For example, the reactivity of hemicellulose is higher for hardwoods than softwoods and, therefore, the degradation zone of cellulose and hemicellulose can be better distinguished in hardwoods (Grønli et al., 2002). Softwood is less thermally stable and decomposed at a wider temperature range compared to hardwood, although a common devolatilisation mechanism could describe the thermal behaviour of both (Grønli et al., 2002). However, additives such as melamine and

nitrogenated adhesives used in wood furniture manufacturing can considerably affect the TG-DTG thermogram of *wood* by lowering the DTG peak temperature due to their inorganic salt content (Moreno and Font, 2015).

Similarly to *wood*, *paper/cardboard* is decomposed in one or two DTG peaks depending on its biochemical composition. The first DTG peak is attributed to degradation of cellulosic matter (200-400 °C) and the second (> 550 °C) is caused by the conversion of paper additives, such as calcium carbonate (CaCO_3), to reaction products (Skreiberg et al., 2011; Chhabra et al., 2019; Cozzani et al., 1995). Grammelis et al. (2009) compared the pyrolytic behaviour of five different types of paper namely magazine paper, cardboard, recycling paper, newspaper and copy paper. These paper samples presented similar profiles of decomposition temperature, but they differed in thermal reactivity (rate of mass loss), with copy paper being the most reactive. A pronounced DTG shoulder was more evident in the DTG thermogram of newspaper compared to other paper samples due to its higher hemicellulose content (Grammelis et al., 2009). Catalytic effects induced by inorganic substances (e.g. ash) and residues from papermaking (e.g. sulphate production process) can also lead to cellulose decomposition at lower temperatures (Sørum et al., 2001).

Textiles may consist of natural or synthetic fibers which correspond to similar thermal behaviour with that of cellulosic and plastic materials, respectively (Cozzani et al., 1995). **Table 2-6** shows that *textiles* are devolatilised into one, two or three main distinct regions (DTG peaks): initial, main and char decomposition (Miranda et al., 2007; Zhu et al., 2004). One DTG peak occurs in purely synthetic or natural fibres, whereas three stages occur in blended fibres. Two peaks are related to natural fibres due to degradation of cellulosic matter. In the first stage (100-300 °C) the mass loss is low, whereas in the second the loss is fast and high (250-400 °C). The third stage is due to the presence of synthetic polymers and/or char formation (380-500 °C) (Chhabra et al., 2019; Zhu et al., 2004; Miranda et al., 2007).

Rubber is a separate waste component category that can be found in SRF/RDF at low proportions, which does not exceed 6% w/w (Velis, 2010; Nasrullah et al., 2016; Stępień et al., 2019). Rubber composition varies depending on the elastomer type, such as nitrile, fluorocarbon, chloroprene,

silicone, polyacrylate, polyurethane, styrene-butadiene (SBR) and natural (Datwyler, 2020). The thermal behaviour of rubber is not described in the present study due to the wide variety of chemical constituents used for its production and its low proportion in SRF/RDF. However, Boumanchar et al. (2017) reported that the decomposition profile of synthetic rubber is similar with that of a plastic mixture consisting of PE, PP and PVC. Information on the thermal stability of rubber can be found elsewhere (Fernández-Berridi et al., 2006; Mathew et al., 2001; Ramesan, 2004; Forrest, 2001; Litvinov and De, 2002; Chhabra et al., 2019; Sircar, 1991; Forrest, 2008).

Table 2-6. Characteristic points of TG-DTG curves (onset temperature (T_o), endset temperature (T_e), number of DTG peak/shoulder, DTG peak temperature (T_p), and residue) of prevalent items/materials in SRF/RDF including *wood*, *paper/cardboard* and *textiles* under specific experimental conditions (gas atmosphere and heating rate) as received reporting basis

Waste category	Waste component	Atmosp. ¹	Heat rate (°C min ⁻¹)	T_o (°C) ²	T_e (°C) ³	No. of peaks	T_p (°C) ⁴	Residue (% w/w) ⁵	Ref.
Wood	Mixed-wood pellets	Inert	5	n.a	n.a	1	348	7	(Skreiberg et al., 2011)
			20			1	370	14	
		Oxidative	5			2	315, 443	< 1	
			20			2	340, 464	< 1	
	Pine-spruce mix	Inert	10	250	500	2	320, 358	7	(Edo et al., 2016a)
		Oxidative	10	287	495	2	350, 470		
	Pine wood	Inert	5, 20, 40	260-280	405-480	2	325-400, 385-450	20	(Williams and Besler, 1996)
	Saw dust	Inert	20	200	420	1	359	18	(Ma et al., 2019)
	Poplar wood	Inert	2 & 5	177	377	2	257, 362	28	(Slopiecka et al., 2012)
			10 & 15	177	467	1	342	26	
	Poplar wood	Inert	10	150	500	2	345, 490	31	(Chen et al., 2015b)
	Hardwood	Inert	5	243	369	1	347	18	(Grønli et al., 2002)
	Softwood			235	375	1	348	23	
	Hardwood	Inert	20	n.a	n.a	1	371-376		

Waste category	Waste component	Atmosp. ¹	Heat rate (°C min ⁻¹)	T _o (°C) ²	T _c (°C) ³	No. of peaks	T _p (°C) ⁴	Residue (% w/w) ⁵	Ref.
	Softwood					1	374-381		(Heikkinen et al., 2004)
Paper/ cardboard	Paper waste	Inert	30	230	600	3	370, 516, 575		(Chhabra et al., 2019)
	Paper waste	Inert	10	300	400	1	350	7	(Chen et al., 2015b)
	Paper*	Inert	20	n.a	n.a	1	361-372	n.a	(Heikkinen et al., 2004)
	Paperboard	Inert	20	200	800	2	361, 732	30	(Ma et al., 2019)
	Glossy paper	Inert	5	n.a	n.a	2	340, > 600	21	(Skreiberg et al., 2011)
			20			2	362, > 600	22	
		Oxidative	5			2	317, > 600	20	
			20			2	337, > 600	23	
	Paper**	Inert	20	300	400	1	365-375	20-26	(Grammelis et al., 2009)
		Oxidative	20	240-260	n.a	1	334-342	5-23	
	Tissue paper	Inert	10	250	400	1	353	7	(Zhou et al., 2015)
	Non-packaging paper waste	Inert	10	200	450	1	325	29	(Silva et al., 2015)
	Newspaper	Inert	3-9	250	400	1	351	n.a	(Lin et al., 1999)
	Toilet paper	Inert	3-9	250	400	1	347	n.a	
Beverage cartoon		Inert	20	200	550	2	373, 488	7	(Grammelis et al., 2009)

Waste category	Waste component	Atmosp. ¹	Heat rate (°C min ⁻¹)	T _o (°C) ²	T _e (°C) ³	No. of peaks	T _p (°C) ⁴	Residue (% w/w) ⁵	Ref.
Textiles	Textile	Inert	30	260	500	2	350, 488	n.a	(Chhabra et al., 2019)
	Cotton clothes	Inert	20	300	410	1	373	10	(Ma et al., 2019)
	Polyester fabrics	Inert	10	375	475	1	438	18	(Chen et al., 2015b)
	Textile waste	Inert	10	200	500	2	330, 440	18	(Silva et al., 2015)
	Textile waste	Inert	1, 5, 10, 20, 40, 60	105-119	433-520	3	199-291, 318 -392, 377-449	10-12	(Muralidhara and Sreenivasan, 2010)
			10	115	474	3	245, 354, 424	11	

¹ Atmospheric conditions: gas used in the TGA experiment; ² onset temperature; ³ endset temperature; ⁴ peak temperature at each DTG shoulder; ⁵ residue: non-volatile matter left after degradation; *included cardboard, corrugated paper, egg carton, facial tissue, glossy paper, newspaper, office paper, paper sludge; ** five types of paper were analysed including magazine paper, cardboard, recycling paper, newspaper and copy paper; n.a: not available

b) Thermal behaviour of prevalent polymers in SRF/RDF

The mechanism for the degradation of plastic polymers is based on the chain scission of macromolecules following a multistep pathway: i) initiation, in which free radicals are formed resulting in a more reactive and unstable polymer; ii) propagation, in which char is formed; and iii) termination, in which inactive by-products are formed via radical coupling or radical disproportionation (Ray and Cooney, 2018). The stage of propagation consists of a series of reactions that involve intramolecular (within a single polymer chain) and intermolecular (between polymer chains) hydrogen transfer followed by the reverse process of polymerization, often referred as unzipping or depolymerisation (Beyler and Hirschler, 2002).

Literature findings showed that the most prevalent post-consumer plastic polymers are PE, PP, PET and PVC. The thermal degradation of these plastic polymers occurs in a single narrow DTG shoulder, except for PVC that consists of two-step degradation during pyrolysis (**Table 2-7**). The thermal stability of polymers in a descending order is as follows: PE > PP > PET > PVC (Lin et al., 1999; Hujuri et al., 2008). In TG-DTG compositional analysis experiments, typically inert gas is preferred, such as nitrogen or argon, to avoid oxidation reactions (Bottom, 2008).

During pyrolytic conditions, PE decomposition starts at 310-450 °C and completes at 460-560 °C in a single DTG peak, depending on its density and the heating rate, whereas the DTG peak temperature occurs in a range of 450-490 °C. Between the most popular types of PE, LDPE and HDPE, the second demonstrates higher thermal stability due to its lower degree of branching (Ray and Cooney, 2018). However, both PE types have quite similar decomposition profiles (Kuźnia and Magdziarz, 2013). PP degradation is quite similar to that of LDPE (Sørsum et al., 2001; Park et al., 2012), although PP has lower thermal stability (Ray and Cooney, 2018; Chhabra et al., 2019) due to the presence of tertiary carbon in the main chain (Beyler and Hirschler, 2002). PP degradation temperatures range from 340-400 °C to 450-520 °C in a single DTG shoulder with a DTG peak temperature between 420 and 490 °C during pyrolysis (**Table 2-7**). Similarly, PET degradation starts at 360-430 °C and completes at 460-550 °C in a single DTG shoulder with a DTG peak temperature ranging from 420 to 465 °C

(**Table 2-7**). In contrast to polyolefins that leave almost zero residue at the end of TGA experiment (< 1% w/w), the residue from PET is nearly 15%. This high residue can be attributed to PET reinforcement with glass fibres, a plastic material widely used in many application areas to improve the strength of PET (Pedersen et al., 2016). The lower stability of PET compared to polyolefins is due to the poor stability of ester bonds in PET chains (Chen et al., 2015b).

PVC decomposition begins at considerably lower temperatures (200-300 °C) (Williams and Williams, 1999) and completes at higher temperatures (500-580 °C) compared to other polymers. The low thermal stability of PVC is attributed to the presence of chloride groups leading to the formation of highly unstable free radicals (Ray and Cooney, 2018). **Table 2-7** shows that the degradation of PVC consists of two DTG peaks during pyrolysis: the first peak (270-380 °C) is due to the release of hydrogen chloride (HCl) (dehydrochlorination stage) and the second (440-470 °C) is due to the degradation of hydrocarbons (Beyler and Hirschler, 2002; Heikkinen et al., 2004). During the stage of dehydrochlorination, nearly 60% of mass loss is induced (Ma et al., 2002) which is almost equal with the Cl content of PVC. Some studies reported three DTG peaks for PVC with the first two peaks slightly overlap (Yang et al., 2001; Yu et al., 2016).

However, the decomposition profile of pure polymers might not fully correspond to the profile of the related plastic items present in SRF/RDF due to cross-contamination leading to lower thermal stability (Silva et al., 2015; Mumbach et al., 2019). Silva et al. (2015) reported that the DTG thermogram, of pure PP differs from this of packaging PP waste, which had a wider range of decomposition temperature with two DTG shoulders instead. Similar results were also found for LDPE films extracted from mixed waste. In addition, Mumbach et al. (2019) compared the thermal behaviour of pure polymers, such as HDPE, LDPE and PP with the respective recovered plastic polymers from the process of recycling paper scrap. Pure polyolefins completely degraded without leaving any residue (< 1% w/w), but recovered polyolefins left considerable amounts of residue due to the presence of impurities and glue materials (Mumbach et al., 2019). The thermal stability of recovered PE was lower compared to pure PE due to impurities, whereas the stability of recovered PP

was higher than this of pure PP (Mumbach et al., 2019). The higher thermal stability of recovered PP could be explained by the presence of biomass materials even at low concentrations.

Părpăriță et al. (2014) reported that the thermal reactivity of PP was increased in PP/biomass composites either due to the behaviour of PP to act as a physical barrier to the volatilization of biomass or due to the reaction of radicals resulting from PP degradation, which otherwise could attack the PP chain, with O-containing structures from lignin degradation (Părpăriță et al., 2014). Despite cross-contamination, the presence of additives in plastic items used to improve the properties of polymers, such as flame retardants, can considerably affect the thermal degradation of plastic materials (Sabet et al., 2019). For example, the addition of 2% w/w nanoglass flakes in PET increases the degree of crystallinity and, therefore, a shift of the degradation zone of PET towards higher temperatures (nearly 10 °C) can be induced (Miri et al., 2019).

Table 2-7. Characteristic points of TG-DTG curves of prevalent fossil-based plastic polymers in SRF/RDF including onset temperature (T_o), endset temperature (T_e), number of DTG peak/shoulder, DTG peak temperature (T_p), and residue under inert atmosphere as received reporting basis.

Polymer	Heat rate (°C min ⁻¹)	T_o (°C) ¹	T_e (°C) ²	No. of peaks	T_p (°C) ³	Residue (% w/w) ⁴	Ref.
PE	3, 5, 7, 9	443	535	1	470	n.a	(Lin et al., 1999)
		425	565		468	n.a	
	2, 5, 10, 20	350	464- 511	1	444- 483	n.a	(Yang et al., 2001)
			497		468	n.a	
	10	310	497		468	n.a	
	10, 20, 30, 40	450	520	1	470	< 1	(Park et al., 2012)
		446	472		464	< 1	
	5	412	474	1	456	14	(Mumbach et al., 2019)
		440	471		466	< 1	
		429	471		455	3	
PE	10-40	408	504	1	463	< 1	(Wang et al., 2020)
PE	10	400	500	1		< 1	(Ray and Cooney, 2018)

Polymer	Heat rate (°C min ⁻¹)	T _o (°C) ¹	T _e (°C) ²	No. of peaks	T _p (°C) ³	Residue (% w/w) ⁴	Ref.
HDPE	10	350	500	1	479	< 1	(Sørum et al., 2001)
	LDPE	n.a	n.a		475	<1	
	10	341	495	1	463	n.a	(Hujuri et al., 2008)
	10	350	500	1	479	< 1	(Sørum et al., 2001)
	LDPE				475		
	10	341	495	1	463	n.a	(Hujuri et al., 2008)
	15	430	519	1	485	< 1	(Yu et al., 2019)
	20	450	550	1	493	n.a	(Heikkinen et al., 2004)
	20	450	550	1	491	n.a	
Isotactic PP	Pure PP	413	451		423	n.a	(Mumbach et al., 2019)
	5			1			
	Recov. PP*	425	456		443	n.a	
	10	340	452	1	486	< 1	(Părpăriță et al., 2014)
	10	350	495	1	437	n.a	(Yang et al., 2001)
	10	337	471	1	446	n.a	(Hujuri et al., 2008)
	10	350	500	1	460	< 1	(Sørum et al., 2001)
	15	390	480	1	447	< 1	(Yu et al., 2019)
	20	420	500	1	472	n.a	(Heikkinen et al., 2004)
PET	PET-bottlers	5, 10, 20, 40, 50	385-425	550	1	427-465	12-14 (Das and Tiwari, 2019)
		5, 10, 15, 25	366-398	514-519	1	430-465	85-95 (Saha et al., 2006)
		5, 10, 20, 40	360-379	460-521	1	419-455	20-22 (Özsin et al., 2019)
		10	370	460	1	441	n.a (Yang et al., 2001)
		10	400	460	1		15 (Ray and Cooney, 2018)
		10	n.a	n.a	1	384	17 (Miri et al., 2019)
		15	430	470	1	433	n.a (Yu et al., 2019)
		20	n.a	n.a	1	444	n.a (Heikkinen et al., 2004)
		30	380	500	1	450	n.a (Chhabra et al., 2019)

Polymer	Heat rate (°C min ⁻¹)	T _o (°C) ¹	T _e (°C) ²	No. of peaks	T _p (°C) ³	Residue (% w/w) ⁴	Ref.
PVC	3, 5, 7, 9	210	530	2	380, 443	n.a	(Lin et al., 1999)
	5, 10, 20, 40	235- 240	515- 578	2	270- 318, ca. 450	10-12	(Özsin et al., 2019)
	10	200	500	3	287, 331, 462	n.a	(Yang et al., 2001)
	10	220	580	2	286, 475	n.a	(Zhou et al., 2015)
	10	200	550	2	290, 450	10	(Sørum et al., 2001)
	15	297	570	2	330, 460	9	(Yu et al., 2019)
	20	260	550	2	305, 467	n.a	(Heikkinen et al., 2004)
	20	300	520	2		n.a	(Erickson, 2007)
Plastic mixture**	10, 20, 30, 40	260	540	2	300, 450	10	(Park et al., 2012)

¹ Onset temperature; ² Endset temperature; ³ Peak temperature at each DTG shoulder; ⁴ Residue: non-volatile matter left after degradation; * Recovered plastic materials from the process of recycling paper scrap; ** Mixture of polystyrene, LDPE, PP and PVC; n.a: not available

The decomposition mechanism of biopolymers involves four main steps: i) cross-linking of biopolymer chains; ii) unzipping of biopolymer chain; iii) devolatilisation and char formation; and iv) further decomposition and depolymerisation (Beyler and Hirschler, 2002). More information on mechanisms and product formation involved during pyrolysis of biopolymers is given by Collard and Blin (2014). Hemicellulose is thermally decomposed first, followed by cellulose and lignin (Beyler and Hirschler, 2002). Xylan is the most commonly used substitute for hemicellulose especially in thermal analysis of waste-derived materials. Depending on the heating rate, cellulose decomposition typically starts at 250-300 °C and is completed at 360-410 °C in a single DTG shoulder, while the DTG peak temperature fluctuates in a range of 320-390 °C (**Table 2-8**). Similarly, xylan degradation

begins at temperatures of 190-250 °C and completes at 250-370 °C in one or two DTG peak, with a DTG peak temperature ranging from 240 to 300 °C, whereas lignin degradation occurs in wider range starting from 100-200 °C to 500-900 °C (**Table 2-8**).

Among the biopolymers, lignin has the lowest rate of mass loss and cellulose has the highest (Quan et al., 2016; Meng et al., 2015a; Yang et al., 2007; Zhang et al., 2016; Lai et al., 2018; Giudicianni et al., 2013; Zhao et al., 2018a; Stefanidis et al., 2014; Chen et al., 2019; Wu et al., 2009). Specifically, the DTG thermogram of cellulose is sharp and narrow due to its homogeneous unbranched structure (Stefanidis et al., 2014), whereas the DTG curve of xylan is slightly shorter (Giudicianni et al., 2013). Two DTG shoulders close to each other during xylan pyrolysis were reported (**Table 2-8**). This first peak might be attributed to the cleavage of bonds between xylan units and the second peak is due to the fragmentation of other depolymerized units (Shen et al., 2010; Quan et al., 2016). The DTG shoulder of lignin tends to have a long tail beyond 500 °C due to the large array of chemical groups (Quan et al., 2016; Brebu and Vasile, 2010). Lignin contains hydroxyl and methoxy branched chains, which can easily break at low temperatures; but, also contains aromatic compounds, which have high thermal stability (Zheng et al., 2019). Lignin degradation usually consists of two DTG peaks, the first is due to cracking of hydroxyl groups in lateral chains (300-380 °C) (Giudicianni et al., 2013) and the second is due to the decomposition of carbonaceous matters (> 650 °C) (Chen et al., 2019).

The highest percentage of mass loss occurs in cellulose degradation and the lowest in lignin degradation (**Table 2-8**). The mass loss of lignin can reach up to 70% at elevated temperatures (ca. 900 °C) indicating its slow carbonization (Yang et al., 2006) due to the presence of cross-linked aromatic molecules (Stefanidis et al., 2014). The higher residue content in xylan compared to cellulose is attributed to the different decomposition mechanisms for the variety of sugar units that compose xylan (Stefanidis et al., 2014).

The thermal behaviour of biopolymers seems to be more variable than that of fossil-based polymers due to their inherent heterogeneous chemical structure. For example, commercial cellulose widely used for experimentation (e.g. microcrystalline cellulose and filter paper cellulose) has higher thermal stability and narrower DTG curves compared to cellulose isolated from biomass materials (Zhang et

al., 2018b; Galiwango et al., 2019) due to different crystallinities (Zhang et al., 2018b; Ramiah, 1970). Xylan is more thermally resistant compared to glucomannan due to different chemical composition, whereas the thermal stability of lignin depends on the isolation method (Ramiah, 1970). In addition, technical lignin contains impurities that depend on the extraction process (e.g. kraft pulping) and biomass source resulting in a variable thermal behaviour and especially charred residue (Sameni et al., 2014). Insights on the thermal behaviour of native lignin are usually obtained by the thermal degradation of biomass materials (e.g. wood), as its structure changes during isolation (Casillas et al., 2018). This is the main reason that **Table 2-8** includes information only on technical lignin.

Table 2-8. Characteristic points of TG-DTG curves of prevalent biopolymers present in SRF/RDF including onset temperature (T_o), endset temperature (T_e), number of DTG peak/shoulder, DTG peak temperature (T_p), and residue under inert atmosphere as received reporting basis.

Polymer		Heat rate (°C min ⁻¹)	T _o (°C) ¹	T _e (°C) ²	No. of T _p (°C) ³ peaks		Residue (% w/w) ⁴	Ref.
Cellulose	MC ⁵	5, 20, 40, 80	300-325	380-430	1	350-390	8	(Williams and Besler, 1996)
	MC ⁵	5	250	350	1	318	18	(Meng et al., 2015b)
	MC ⁵	5	327	407	1	337	n.a	(Giudicianni et al., 2013)
	MC ⁵	10	315	400	1	355	7	(Yang et al., 2007)
	MC ⁵	10	310	390	1	360	12	(Wu et al., 2009)
	MC ⁵	10	n.a	n.a	1	343	21	(Zhou et al., 2015; Meng et al., 2015a)
	MC ⁵	10	300	400	1	344	9	(Zhou et al., 2015)
	MC ⁵	10	300	400	1	335	10	(Zhang et al., 2016)
	MC ⁵	10	300	400	1	344	9	(Long et al., 2016)
		10	257	405	1	335	5	(Zhao et al., 2018a)
	MC ⁵	10	300	400	1	335	n.a	(Chen et al., 2019)
	MC ⁵	20	300	400	1	350	8	(Lai et al., 2018)
	MC ⁵	20	280	360	1	339	7	(Stefanidis et al., 2014)

Polymer	Heat rate (°C min ⁻¹)	T _o (°C) ¹	T _e (°C) ²	No. of peaks	T _p (°C) ³	Residue (% w/w) ⁴	Ref.	
α-cellulose	20	260	410	1	375	16	(Quan et al., 2016)	
Xylan	3, 10, 20, 80	185-214	354-369	2	234-273, 267-304	n.a	(Shen et al., 2010)	
	5, 20, 40, 80	250-290	320-400	1	285-325	20	(Williams and Besler, 1996)	
	5	227	n.a	2	247, 333	n.a	(Giudicianni et al., 2013)	
	10	220	315	1	268	20	(Yang et al., 2007)	
	10	200	340	2	245, 285	n.a	(Chen et al., 2019)	
	10	210	320	1	290	45	(Wu et al., 2009)	
	10	n.a	n.a	2	250, 274	23	(Meng et al., 2015b; Meng et al., 2015a)	
	10	200	350	2	245, 296	27	(Zhou et al., 2015)	
	10	200	350	2	240, 290	20	(Zhang et al., 2016)	
	10	200	350	2	245, 296	27	(Long et al., 2016)	
	20	210	370	2	210, 370	14	(Quan et al., 2016)	
	20	200	320	2	246, 295	25	(Stefanidis et al., 2014)	
	20	200	250	n.a	283	27	(Wang et al., 2013)	
	20	190	400	2	250, 300	20	(Lai et al., 2018)	
Lignin	Klason	5, 20, 40, 80	300	430-530	1	380-460	55	(Williams and Besler, 1996)
	Alkali	5	n.a	n.a	1	363	n.a	(Huang et al., 2011)
	Alkali	10-40	194	900	1	361	47	(Wang et al., 2020)
	Alkali	10	160	900		n.a	46	(Yang et al., 2007)
	Alkali	10	200	550	1	352	65	(Wu et al., 2009)
	Alkali	10	220	800	2	300, 680	45	(Zhang et al., 2016)
	Alkali	10	200	600	1	340	54	(Quan et al., 2016)
	Alkali	10	210	520	1	315	48	(Zhao et al., 2018a)
	DL ⁶	10	138	780	2	350, 763	43	(Chen et al., 2019)

Polymer	Heat rate (°C min ⁻¹)	T _o (°C) ¹	T _e (°C) ²	No. of T _p (°C) ³ peaks	Residue (% w/w) ⁴	Ref.
DL ⁶	10	n.a	n.a	2	342, 764	40 (Meng et al., 2015a; Meng et al., 2015b)
DL ⁶	10	200	800	2	337, 768	46 (Zhou et al., 2015)
DL ⁶	10	200	800	2	338, 768	46 (Long et al., 2016)
Klason	20	200	500	1	387	n.a (Cabeza et al., 2015)
Alkali	20	200	550	1	325	55 (Lai et al., 2018)
Kraft	20	105	800	1	350	34 (Ibrahim et al., 2011)
Kraft	20	140	600	1	380	41 (Stefanidis et al., 2014)
Soda	20	105	800	1	360	37 (Ibrahim et al., 2011)
*		200	500	2	280-390, ca. 420	(Brebú and Vasile, 2010)

¹ Onset temperature; ² Endset temperature; ³ Peak temperature at each DTG shoulder; ⁴ Residue: non-volatile matter left after degradation; ⁵ Microcrystalline cellulose; ⁶ Dealkaline lignin produced from the dealkalization of papermaking black liquid; * Derives from a review paper on the typical degradation of lignin during pyrolysis; n.a: not available.

c) *Interaction effects between waste materials*

Interaction effects between two or more materials occur when the total effect produced by the blend of these materials is higher (synergy) or lower (antagonism) than the sum of the individual materials (Farrow et al., 2013). It has been reported that the interaction effects between waste components are negligible during TGA experiments (Skodras et al., 2009; Cozzani et al., 1995; Heikkinen et al., 2004; Danias and Lioudakis, 2018). In that case, the thermal behaviour of a mixture can be described using the weighed sum method (WSM). According to WSM ‘*the thermal degradation curve of a mixture is equal to the sum of contributions of the corresponding individual components*’ (Heikkinen et al., 2004):

$$Y_{\text{mix}} = x_1y_1 + \dots + x_ny_n \quad \text{Eq. 2-1}$$

Where: Y_{mix} is the approximated mass loss rate of the mixture, x_i is the proportion of i component in the mixture, y_i is the mass loss rate of i component and n is the number of components.

WSM has been reported as a useful tool for the quantification of waste composition (Cozzani et al., 1997; Cozzani et al., 1995) or for the estimation of waste devolatilisation based on the thermograms of waste components (Heikkinen et al., 2004; Lin et al., 1999). Despite above claims, evidence of interactions amongst waste components (items, materials, chemical compounds) exists. Grammelis et al. (2009) reported that the decomposition rate of RDF is higher than those of individual waste components. Interaction between PVC and cellulose in the form of cotton or tissue paper was noticed by many researchers (Sørum and Task, 2001; Grammelis et al., 2009; Ma et al., 2019; Matsuzawa et al., 2001; Yu et al., 2016; Zhou et al., 2015). Specifically, the released HCl from PVC reacts with cellulose increasing biomass reactivity.

Interactions among biomass components (Akubo et al., 2019; Jaffar et al., 2020; Cabeza et al., 2015; Hosoya et al., 2007) and between biomass and fossil-based plastics (Özsin et al., 2019; Wang et al., 2020) were identified through kinetic and compositional analysis of pyrolysis products using TGA-EGA. Zhao et al. (2018a) reported that the presence of lignin reduced the pyrolysis rate of cellulose, whereas the presence of cellulose and hemicellulose promote the production of more phenolic substances during lignin pyrolysis. In addition, Long et al. (2016) reported that the formation of char from xylan at low temperature induced the inhibition of heat and mass transfer processes of cellulose. In contrast, other researchers found the interaction amongst biomass components as insignificant (Cao et al., 2019; Raveendran et al., 1996).

Interactions among plastic polymers were also identified. For example, Williams and Williams (1999) reported that plastic mixtures had higher yield of pyrolysis products compared to the yields of the single plastics. Singh et al. (2019) found that the thermal degradation of a plastic mixture (HDPE, PP, PET and PS) started earlier and the rate of mass loss was considerably lower than the degradation of individual polymers. So far, no clear evidence whether considerable interaction effects occur

between waste materials and therefore the use of WSM might be controversial for compositional analysis of waste-derived materials through TG-DTG.

2.4.3 Chlorine content in SRF: a limiting technical factor

The Cl content in SRF affects the technological performance and therefore the maintenance, operating and capital costs and generally the economic efficiencies of end-user applications (Deans et al., 2016; Gehrmann et al., 2009). These operating problems are affected not only by the concentration of total Cl (Total [Cl]) in SRF but also by the availability or volatility of Cl during thermal treatment (Pettersson et al., 2009). This problem is eliminated when plants operate at low steam temperatures leading to lower energy efficiency (Miller and Tillman, 2008). For example, the efficiency of the MSW-fired power generation is less than 15% in order to avoid high-temperature corrosion caused by HCl gas (Wang et al., 2002).

A high-quality SRF, with constant composition and low Cl content, is a prerequisite for increased substitution rates of fossil fuels by SRF (Pomberger and Sarc, 2014). This can be achieved, to a certain degree, by using well selected waste feedstock and suitable sorting technologies employed in MT/MBT, such as near infra-red (NIR), to remove Cl containing compounds (Cuperus, 2011; Lechtenberg and Diller, 2012). To date, relevant research has focused on generic QA during SRF production (Velis et al., 2010), Cl in SRF produced in MT/MBT plants (Velis et al., 2012), review of Cl fate in incineration, gasification, and pyrolysis (Lu et al., 2018) and in generic use of alternative raw materials and fuels in cement kilns (Uson et al., 2013). But, despite its commercial importance, the role of Cl stemming from SRF is still poorly understood.

2.4.3.1 A Cl categorization – where [Cl] load comes from?

Total [Cl] in SRF can be differentiated based on two criteria. First, chemical speciation of Cl, which can largely be grouped as Cl chemically bound in *organic* or *inorganic* compounds; this split can often be coupled with the MCP waste category, assuming just one prevalent form of chemical compound per MCP category. Second, in the literature the fate of Cl in the solid and gaseous phase

during thermal treatment has also been used to classify it as '*incombustible*' or '*combustible*'. The relevance of these two categories is described below.

a) Chlorine categorization based on chemical compound/ material of origin

Chlorine can be identified as *organic* and *inorganic*, depending on its chemical bonding, which often correlates with the type of waste material (origin). The main source of *organic* Cl in SRF is plastics, whereas *inorganic* Cl derives from food waste: e.g. sodium chloride (NaCl) (common table salt) (Guo et al., 2001; Ma et al., 2010). The characterization of Cl as *water soluble* and *water insoluble* may often indicate the presence of *inorganic* and *organic*, respectively (Vainio et al., 2013), although it might be misleading, as some *organic chlorides* in SRF might be moderately soluble in water (Domalski et al., 1986), such as epichlorohydrin (EPI) (Open Chemistry Database, 2019a) and dichloromethane (DCM) (Open Chemistry Database, 2019b).

A main contributor to [Cl] load in MSW and sub-fractions is PVC, with Total [Cl] nearly 46 – 56% w/w (ECN Phyllis, 2019): a therefore unwanted polymer in SRF leading to high HCl release during fuel combustion (Heikkinen et al., 2004; Wang et al., 2002). Ma and Rotter (2008) reported that 63-72% of the entire [Cl] load in MSW derived from plastics is due to a considerable proportion of PVC in the *plastic* fraction. This is in agreement with Watanabe et al. (2004) suggesting that the contribution of plastics to the [Cl] load in MSW was 63% and with Riber et al. (2009) reporting that the non-recyclable plastic fraction constituted 60% of [Cl] load in household waste. Similarly, Velis et al. (2012) stated that *plastic film* and *packaging plastic* contributed 62% of total [Cl] load in SRF and Burnley (2007) claimed that 48% Total [Cl] in MSW was stemming from *plastics*.

However, numerous *organic* Cl-containing compounds, other than PVC, are also used in many consumer products, delivering specific functionality (**Table 2-9**). Nearly one third of industrially produced Cl each year is predefined for PVC production, whereas a comparable amount goes to the production of isocyanates and oxygenates, prevalent chemicals in the packaging and textile industry (Deans et al., 2016). So despite the literature having been preoccupied with identifying/removing the

presence of PVC in SRF, a considerable load can be ascribed to other sources, either of lower [Cl] or in less prevalently used materials.

For example, polyvinylidene chloride (PVdC) has a higher [Cl] than PVC (nearly 71-73% w/w (Bhaskar et al., 2006; Zhao et al., 2018b)) and is typically used in packaging products; often combined with more affordable plastics, such as PP for higher strength and moisture resistance (Marsh and Bugusu, 2007). Carbonyl dichloride (phosgene) is extensively used in the production of polycarbonate, which is used for glass replacements in items such as food containers, water and sterilisable baby bottles (Marsh and Bugusu, 2007), and isocyanates, which are precursors for the production of polyurethanes (Twitchett, 1974). Polyurethanes are present in various consumer products, such as furniture, clothing, shoes, electrical devices, sealants and adhesives (Krone et al., 2003; ECI, 2019), eventually becoming MSW.

Organic Cl can also be present in MSW in the form of EPI, a compound used in the production of elastomers in rubber production, making synthetic rubber a significant potential contributor of [Cl] load, as verified by previous researchers (Velis, 2010; Velis et al., 2012; Nasrullah et al., 2016). Velis et al. (2012) investigated the properties of components in commercially produced SRF and identified that almost 14.5% of total [Cl] load in SRF was attributed to ‘shoes’, concluding that synthetic rubber within shoes constitute a highly chlorinated waste component and should therefore be separated out from the SRF. The Total [Cl] of shoes was found in a range of 3.6-6% w/w_d (Velis, 2010; Rotter et al., 2004). EPI is also used for the manufacture of epoxi resins, which are mainly used in packaging and paper manufacture (Santodonato et al., 1980), in insulation of electronic equipment, in adhesives and fibre-reinforced composites (Barton, 1985). For that reason, SRF item components, categorized as ‘adhesives’, ‘furniture’ and ‘cables’, are also considered as potential high sources of Cl. For example, Velis (2010) measured the Total [Cl] of ‘cables’, considered as electric wires with variable plastic casing, close to 2.5% w/w_d.

Yet other sources of *organic* Cl, occurring less frequently in MSW, contribute to the overall [Cl] load. For example, chlorinated polyethylene (CPE) is a thermoplastic elastomer produced by the chlorination of PE with advanced properties (ViaChemical, 2017), finding its way typically into

mixed unsorted or residual MSW. In addition, DCM and tetrachloroethene (TCE) are chlorinated solvents with various applications, as well (**Table 2-9**).

Inorganic Cl, consisting of alkali metal chlorides such as NaCl, potassium chloride (KCl), calcium chloride (CaCl_2) (**Table 2-9**), is prevalent in the ‘food waste’ fraction. The high proportion of ‘food waste’ in MSW makes NaCl the major contributor to the [Cl] load in MSW (Ma et al., 2010; Guo et al., 2001; Wu et al., 2016). But, *inorganic* Cl is not entirely present only in ‘food waste’. Ziegler-Natta catalysts used in the polymerization of polyolefin are composed of trichlorotitanium (TiCl_3) and magnesium chloride (MgCl_2) leading to the presence of Cl in polyolefin plastic (Shamiri et al., 2014). Additionally, packaging components, such as plastic bottles of chlorinated detergents, may often contain remnants of chloride compounds such as sodium hypochlorite (NaClO) – the most common chloride used for bleaching (Zoller, 2008).

Chlorine dispersion in various waste components restricts the ability to reduce the [Cl] in SRF below a limit depending on waste composition (Rotter et al., 2004). But, the technological performance of SRF can be improved by increasing the mass fraction of waste components that contain negligible amounts of Cl such as *paper/cardboard*, *wood* and *non-PVC plastics* (Nasrullah et al., 2016).

Paper/cardboard is a main component in MSW with low [Cl] contributing considerably to reducing the overall [Cl] load in SRF as reported by Velis (2010). The low [Cl] in paper is due to residuals of chlorine dioxide (ClO_2) and hypochlorite (ClO^-) may remain in paper after the bleaching process (Bajpai, 2014).

Nevertheless, such components can be contaminated with chlorides due to the absorption of water percolated through food waste in the residual waste stream (cross-contamination) (Uchida et al., 1988), e.g. in a high compaction collection vehicle, which is a prevalent collection means for residual MSW in developed countries (Edjabou et al., 2015). Domalski et al. (1986) reported that in MSW where ca. 45% w/w was ‘paper’, 65-80% of the entire *inorganic* [Cl] load could be allocated to ‘paper’. Cross-contamination is a partly unavoidable condition, which can decrease the market value of SRF or even make waste fractions unsuitable for further processing (Smith et al., 2009). Cross-contamination of SRF from residuals might occur at different stages of waste processing- not only

during waste collection. Despite the beneficial role of shredding in waste homogenization (**Section 2.5.1**), over-pulverization may lead to considerable cross-contamination and, therefore, should be avoided (Velis et al., 2010). The level of cross-contamination can decrease if the performance of sorting unit operations in an MT/MBT plant, which can be evaluated by the purity, recovery rate and yield factor, is high (Velis et al., 2010; Riddell et al., 2015).

Table 2-9. Main compound forms and MCPs applications of organic and inorganic Cl in SRF.

Cl type	Name	Symbol	Formula ⁽¹⁾	Uses	Ref.
Organic	Ethylene dichloride	EDC	$C_2H_4Cl_2$	VCM production	(Kurtz, 1975)
	Chloroethene	VCM	C_2H_3Cl	PVC production	(Summers, 2000)
	Polyvinyl chloride	PVC	$(C_2H_3Cl)_n$	Tubes, pipes, films, toys, flooring, and other construction production; packaging industry; textiles	(Summers, 2000)
	Polyvinylidene chloride	PVdC	$(C_2H_2Cl_2)_n$	Packaging of cheese, tea, coffee, poultry and meat products, catsup and salad dressing bottles; textiles	(Marsh and Bugusu, 2007)
	Epichlorohydrin	EPI	C_3H_5ClO	Textiles and rubber (elastomer production); coating of food and beverage cans, plastics, cables, adhesives and fibre-reinforced composites (epoxy resin production); paper products (tissues, towelling, and beverage filters)	(Barton, 1985; Santodonato et al., 1980)
	Chlorinated Polyethylene	CPE	$(C_2H_3Cl)_n^*$	Cable jacketing, rubber, roofing, automotive and industrial hose and tubing, moulding, base polymer	(ViaChemical, 2017)
	Dichloromethane	DCM	CH_2Cl_2	Paint removal; textiles, shoes, adhesives, cables and furniture (polyurethane foam production); decaf coffee	(Belay et al., 2008; Kaefferlein et al., 2011; Jimoda, 2011)

Cl type	Name	Symbol	Formula ⁽¹⁾	Uses	Ref.
	Tetrachloroethene	TCE	C ₂ Cl ₄	Textiles; cleansers; adhesives and waterproof materials	(US Department of Health and Human Services, 2019a; Hickman, 2000)
	Carbonyl dichloride (Phosgene)	CG	COCl ₂	Textiles, shoes, adhesives, cables, furniture (polyurethane foam production); glass container and bottles	(Marsh and Bugusu, 2007; Twitchett, 1974)
Inorganic	Sodium hypochlorite		NaClO	Most common chloride bleach	(Zoller, 2008)
	Sodium chloride		NaCl	Table salt	(Guo et al., 2001; Ma et al., 2010; Themelis, 2010)
	Titanium (III) chloride		TiCl ₃	Ziegler-Natta catalysts for PP and PE polymerization	(Shamiri et al., 2014)
	Magnesium chloride		MgCl ₂		
	Potassium chloride		KCl	Food processing (flavouring agent, nutrient supplement, pH control agent, stabilizer and thickener)	(Van Buren et al., 2016)
	Calcium chloride		CaCl ₂	Food additives (canned vegetables and fruits, cheese, beverages and ice cream)	(US Department of Health and Human Services, 2019b; Keowmaneechai and McClements, 2002)

* (Manaila et al., 2012), ⁽¹⁾ (ChemSpider)

b) Chlorine categorization based on its fate (partitioning) in WtE combustion

The fate of Cl in thermal processing has been more extensively studied for WtE plants than cement kilns. This is in agreement with a review study that indicated the minimum attention by researchers paid to co-combustion in cement-kilns compared to waste incineration (Astrup et al., 2015). Hence, the relevant literature was considered to obtain insights on the combustion behaviour of Cl and its species. Based on the fate of Cl in thermal processing, the proportion of Cl converted into HCl in the flue gas during combustion, could be considered to be a ‘*combustible*’ fraction, while the proportion that remains in incinerator bottom ash (IBA) considered as ‘*incombustible*’ (Watanabe et al., 2004).

Such terminology is based on Cl fate within a particular system – that of WtE combustion plants, practically defined as the partitioning coefficients, calculated as part of material flow analysis, widely applied for metals (e.g. (Brunner and Monch, 1986)), often interpreted in relation to their volatility (e.g. volatile vs. lithophilic elements or compounds). An association between Cl abundance and metal partitioning behaviour has been reported (Saqib and Bäckström, 2014), with the presence of Cl decreasing the transfer of trace elements to bottom ash by forming highly volatile metal chlorides. Specifically, elevated Cl levels led to an increased distribution of highly (Hg, Cd) and moderately (Pb, Zn, As) volatile chlorides to fly ash due to the affinity between trace elements and HCl released during combustion. This is also confirmed by earlier studies (Belevi and Moench, 2000; Astrup et al., 2011).

Investigations on the fate of Cl during waste combustion in incinerators (older MSW combustion plants without energy recovery) and WtE boilers indicated that HCl is an important product (Wang et al., 2002; Uchida et al., 1988; Kanters et al., 1996). MSW combustion in a fluidized bed reactor at high temperature (900°C) resulted in ca. 45% w/w of Cl load partitioning to the gaseous phase and 55% w/w to the solid phase (Liu et al., 2000). Chang and Huang (2002) investigated the Cl speciation and material flow in two MSW incinerators with different air pollution control equipment: the first was equipped with cyclone, followed by a dry lime scrubbing system with a fabric filter; and the second was equipped with an electrostatic precipitator followed by a wet scrubber. They found that ca. 60% w/w of the total Cl input at both incinerators was captured by the air pollution control devices, while the remaining discharged into IBA.

Research into the correlation between the *organic* vs. *inorganic* bonding of Cl in compounds and its fate in thermal processing has been carried out. Ma and Rotter (2008) proposed that *organic* and *inorganic* Cl may present different thermal behavior. During combustion major products of *inorganic* Cl are HCl, Cl₂ and salt depositions, whereas *organic* Cl contributes more to the HCl release. This relative contribution is due to either incomplete decomposition of NaCl (*inorganic* Cl) leading to Cl deposition in IBA and/or slower release rates of Cl ions that might promote the potential formation of metal chlorides (Wang et al., 1999; Wang et al., 2002; Wey et al., 2006). Wang et al. (2002)

compared the amount of HCl released by NaCl compared to PVC, finding that the HCl conversion rate of total Cl input from PVC was between 60 and 65%, whereas the same conversion rate from NaCl was in a range of 30-40%. A possible reason was that PVC contains hydrogen which reacts with Cl forming HCl, while NaCl reacts with water vapour to produce HCl. Another consideration was that the affinity of Cl to sodium is higher than of Cl to hydrogen (Wey et al., 2001).

Material flow analysis of Cl during MSW combustion showed that *organic* Cl contributes considerably to the formation of *combustible* Cl. Watanabe et al. (2004) reported 75% of *organic* Cl in input material resulted as *combustible* and 25% as *incombustible*. Almost 100% of Cl in PVC is irreversibly transformed into HCl and released at a temperature range of 200-400°C, regardless of the operating conditions of the combustion process (e.g heating rates), making PVC a crucial precursor of HCl formation (Lu et al., 1996; Ma and Rotter, 2008); **(Reaction 2-1)** (Kaufmann, 1997). Kanter et al. (1996) combusted MSW with and without the PVC fraction and deduced that the removal of PVC materials from MSW could decrease HCl release by up to 40%.



However, Ma et al. (2010) suggested that the correlation between *organic-inorganic* and *combustible-incombustible* Cl content is not robust, because Cl volatilization is affected, also, by the temperature profile of the reactor. This is in agreement with Wey et al. (2006), who investigated HCl formation during waste incineration in a fluidized bed reactor and showed that 63.5%, 98.7% and 87.5% of *organic* Cl was transformed into HCl at 600°C, 700°C and 800°C, respectively.

Despite the inability to clearly associate Cl categorization into *combustible* and *incombustible* to physico-chemical properties of MCPs or to combustion processing conditions, this distinction may be of operational relevance for WtE plants. However, it may not be entirely suitable to extrapolate combustion results from WtE technological settings to cement plants with regards to the fate of Cl during combustion, because the processes, reactions and sinks are customarily more complicated in the latter (Potgieter, 1997).

2.4.3.2 Reactions and implications of Cl in SRF co-combusted in cement kilns

Modern cement plants – cyclone preheater/precalciner kilns – are the main end-users of SRF (ERFO, 2019), but Cl is one of the key limiting factors (Cuperus, 2011; Lechtenberg and Diller, 2012; Pomberger and Sarc, 2014). Whereas for WtE boilers there is ample information on the implications and fate of Cl during combustion of solid waste (Liu et al., 2000; Chen et al., 2015a; Albina and Themelis, 2005; Pettersson et al., 2013; Hilber et al., 2007a), the situation has not been extensively studied in the cement industry. This is despite the preoccupation of the cement off-takers with Total [Cl] in SRF. The main difference between the two combustion technologies is that cement plants operate at higher temperatures, with clinkering taking place at 1450°C, and with temperatures of 2000°C in the flame of the main burner and 900-1200°C in the precalciner (Jensen, 1999; Cement Sustainability Initiative, 2005). A typical bed temperature in EfW boilers fluctuates between 780-900°C (Miller and Tillman, 2008).

The 'raw meal' used as feedstock for the clinker production comprises primarily limestone and clays, providing a source of silicates and aluminates, plus some iron oxides (Fe_2O_3) (Schorcht et al., 2013). Limestone has a high absorption capacity of acidic gases (e.g. HCl) due to its alkalinity and high content of reactive calcium oxide (CaO) – often referred to as free lime, which has high affinity for Cl (Karstensen, 2006; Lanier et al., 1996). This may importantly push the [Cl] in the cement over the 0.1% w/w threshold stipulated in related CEN standard (EN197-1, 2000). For that reason, the output quality of clinker must be well monitored to detect any effects when SRF is used (Schorcht et al., 2013).

a) Chlorine circulation in a kiln-preheater system

In a modern cement kiln, Cl is volatilized and is returned with the flue gas back to the preheater, where it condenses and returns to the high temperature zone, creating a continuous volatilization-condensation reaction. This can cause instability in the system and increase the energy consumption (Enders and Haeseli, 2011). Chlorine volatilization takes place in the burning zone of the kiln at a temperature range of 900°C to 1200°C (Enders and Haeseli, 2011), while condensation occurs in the riser pipes and in the lower cyclones of the preheater (Cortada Mut et al., 2015). Thus, at

temperatures between 700°C and 900°C, mixtures with low melting points are formed (Schorcht et al., 2013). The material and the hot-gas flows in the kiln are arranged in counterflow, causing Cl circulation (**Figure 2-2**), that can be controlled by reduced [Cl] in fuel and raw materials, and/or installation of a bypass system (Enders and Haeseli, 2011) – a technical system that reduces incrustations through chlorides removal (Ernst-Michael-Sipple and Muellner, 2015). Chlorine circulation is determined by the phase equilibrium between liquid and gaseous alkali metal chlorides (Cortada Mut et al., 2015; Enders and Haeseli, 2011). Also, a high sulfur trioxide (SO_3) to alkali ratio is crucial for Cl cycling/circulation, as sulfation of alkali chlorides may occur at temperatures above 900°C (Cortada Mut et al., 2015).

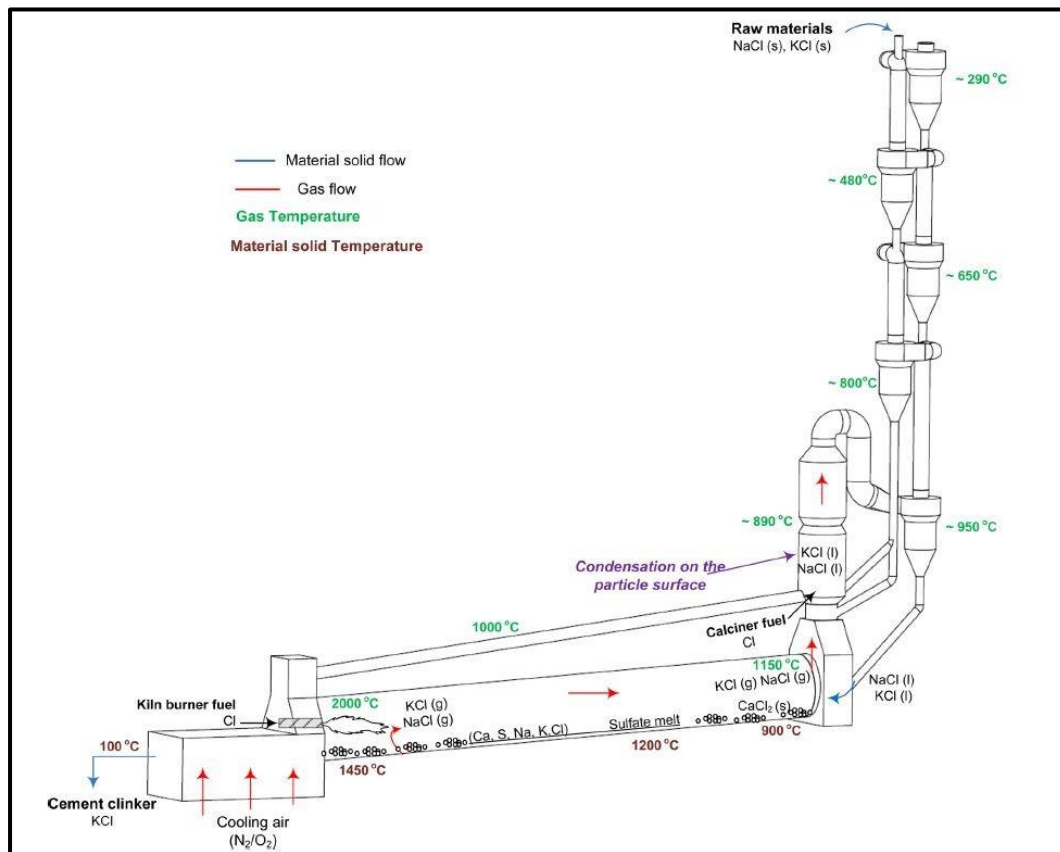


Figure 2-2. Chlorine circulation in a modern cement kiln: Cl volatilization occurs in the burning zone at a temperature range of 900°C to 1200°C and Cl condensation occurs in the lower cyclones of the preheater forming mixtures with low melting points, which return to the high temperature zone, creating a continuous volatilization-condensation reaction. Adopted by Cortada Mut et al. (2015).

Chlorine vaporization can take place via two mechanisms. In the first mechanism inorganic chlorides are volatilized directly in the gas phase without intermediate reactions due to high temperatures, as follows (Enders and Haeseli, 2011):



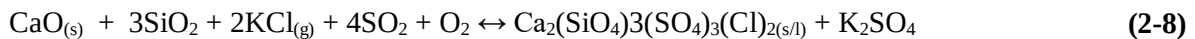
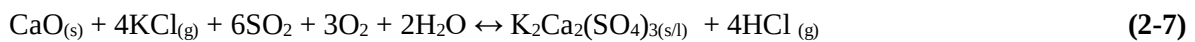
Also, organic Cl can be volatilized as HCl (**Reaction 2-1**) and/or alkali chlorides react with water vapours in the gas phase at temperatures above 1000°C, forming HCl thus (Cortada Mut et al., 2015; Saint-Jean et al., 2005):



In the second mechanism, HCl reacts with silicate minerals and melts forming alkali chlorides in the flue gas (Enders and Haeseli, 2011):



Condensation products are minerals derived from the reactions between alkali chlorides in gas phase and ingredients of the raw meal (Enders and Haeseli, 2011):



b) Operating problems induced by the presence of Cl in modern cement kilns

Chlorine-related problems in cement kilns are attributed to Cl circulation associated with cement kiln dust (CKD) recycling and Cl absorption from free lime. This phenomenon can lead to sticky particles generating material build-ups on the wall (Cortada Mut et al., 2015). Build-ups are formed on the preheater cyclones due to excessive Cl circulation (Holderbank, 1992) causing blockages (Cortada Mut et al., 2015; Karstensen, 2006), and pressure drops in the preheater tower (Turnell, 2001). In addition, the presence of Cl can induce problems in the equipment of air pollution control equipment.

An insulating layer can be formed on the electrodes in the electrostatic precipitator reducing the electric field and, thus, lowering its capture efficiency, leading to increased dust emissions (Schorcht et al., 2013). Enders and Haeseli (2011) reported that [Cl] in raw meal can serve as an indicator to evaluate the risk of build-up formation, suggesting a [Cl] more than 3.5% w/w is detrimental.

Successive deposition of particles and gas condensation may cause ring formation (Dominguez et al., 2010) leading to high cleaning costs and kiln shutdowns (Schorcht et al., 2013). Ring formation enhances Cl circulation since the available opening of the kiln for the gas and material flow decreases (Tran and Barham, 1991; Enders and Haeseli, 2011).

Corrosion potential in cement kilns is complicated due to multiple temperature zones, plus variable numbers of preheaters and raw meal composition (Potgieter, 1997). Low levels of oxygen in combination with high [Cl] input may cause corrosion of the kiln shell, resulting in thinning below the mechanical limits of kiln shell stability (Enders and Haeseli, 2011; Cortada Mut et al., 2015). Yet evidence suggests that the corrosion mechanism in cement kilns is similar to those in steam boilers (Potgieter et al., 2004; Jons and Ostergard, 1999).

The corrosion mechanism can be described by a number of chain reactions: alkali chlorides react with metal oxides (**Reaction 2-9a**) or HCl is oxidized (**Reaction 2-9b**), forming Cl₂, which reacts with the iron metal shell (**Reaction 2-10**). These products are oxidized and hydrolysed forming metal oxides and HCl (**Reaction 2-11 and 2-12**) (Lee et al., 2007; Sharobem and Castaldi, 2012; Cortada Mut et al., 2015):



* Sodium can be replaced by potassium

c) *Mitigation of Cl-related problems in cement kilns*

From a technical perspective, high SRF quality can be achieved by producing a homogeneous waste output with low Total [Cl]. There are actions and processes that can be applied to assure SRF quality regarding Cl-related problems in the stage either of pre-processing or co-combustion. **Table 2-10** summarises the main measures that can be taken for mitigating Cl-induced problems at both stages.

Table 2-10. Measures for mitigation of Cl-related problems during pre- and co-processing of SRF in cement kilns.

Measures	Description	Demerits	Reference
Pre-processing	Near-infra-red (NIR)-sorting technology	Optical sorting technology that enables plastic materials to be separated by polymer type (used for sorting out the PVC fraction).	Difficulty to treat cost-efficiently dark plastic components and incapability to sort out <i>inorganic</i> Cl. (Sarc et al., 2014; Pomberger and Sarc, 2014; Velis et al., 2012; Morrish et al., 2010)
	Selective collection	Pre-treatment of MSW for direct extraction of PVC-containing materials.	No clear evidence whether different types of selective collection are more efficient than mechanical processing in dedicated MT/MBT plants. (Rada and Ragazzi, 2014)
	Addition of low Cl-containing materials	Increasing the mass fraction of paper and cardboard due to its biogenic content and lower [Cl].	Decrease of SRF calorific value and consequently its financial attractiveness. (Velis et al., 2012; Velis et al., 2010)
	Torrefaction	Conversion of SRF into a coal-like material (char) at low temperature (200-350°C) leading to the improvement of SRF quality. The fuel becomes more homogeneous and its calorific value can be increased from ca. 20 to 25 MJ/kg improving the SRF attractiveness as an energy source, whereas Total [Cl] can decrease by 35 to 55% due to Cl migration from feedstock to the gas phase.	No commercial torrefaction unit is available yet. (Edo et al., 2016b; Białowiec et al., 2017; Wild et al., 2016)

Measures	Description	Demerits	Reference
	Hydrothermal treatment	A reaction of alkali metals with organic chlorides under high temperatures, producing inorganic Cl, which can be water washed and dewatered reducing [Cl] and retaining the calorific value of the fuel.	Removes only <i>organic</i> Cl and increases the production cost of SRF. (Prawisudha et al., 2012)
	Optimization of waste processing unit operations in MT/MBT plants	Efficiency of mechanical unit operations is far from perfect and optimization of material flow, waste sorting, transportation, storage and safe handling of the materials from the source to final treatment is required	So far, optimization of sorting processes requires more energy demanding plant configurations, adversely affecting sustainability. MT/MBT plants need an economic incentive policy. (Hinkel et al., 2019; Fei et al., 2018; Bayard et al., 2015; Velis et al., 2010)
Co-processing	Operating improvements	Minimization of gas temperature fluctuations, enhancement of gas mixing with gas recirculation, sufficient residence time and combustion temperature	Hard to achieve when highly inherent heterogeneous materials are used as co-fuels. (Lee et al., 2007; Schorcht et al., 2013; Rademakers et al., 2002)
	Co-combustion at a conservative substitution rate	Depending on the fuel quality and compatibility of SRF properties with the thermal recovery process (50% is a realistic value for cement kilns)	Less cost-effective solution than the optimum rate. (Velis et al., 2010; Gendebien et al., 2003)
	Installation of Cl-bypass system	A technical system that reduces incrustations through chlorides removal	High investment cost, which indicatively can reach 5 million US\$. (Lechtenberg and Diller, 2012; Enders and Haeseli, 2011; Ernst-Michael-Sipple and Muellner, 2015)

In **Table 2-10**, the measures have their merits and demerits, but it is not easy to address the best option. The effectiveness of each depends on the quality and quantity of input waste feedstock and the existing framework conditions at municipal level (Hinkel et al., 2019). A combination of these measures could bring synergistic effects, whereas QA procedures are undoubtedly required.

Maintaining constant operating conditions during thermal treatment and optimizing mechanical processes employed in MT/MBT plants could ensure SRF QA.

2.5 QA measures for SRF product quality

In the stage of post-production, the establishment of a QMS ensures that SRF characterization was carried out under a control manner following a documented validated method (Barwick, 2016). QC examines the quality of SRF product and checks if quality requirements are fulfilled, while QA provides confidence in analytical measurements indicating that results are valid under an acceptable level of uncertainty (CITAC, 2002). Noted that QA does not 100% guarantee the reliability of analytical results, especially in heterogeneous samples such as SRF, but it considerably reduces quality failures to an acceptable level (CITAC, 2002).

Quantifying and harnessing SRF variability to ascertain efficient utilization (Flamme and Geiping, 2014) remains a major challenge for turning waste materials into secondary resources, and therefore a key barrier to a genuine circular economy (Esbensen and Velis, 2016). Special attention should be paid to single aspects of the post-production QMS including sampling, chemical analysis and statistical descriptors (Velis et al., 2010). In order SRF be able to meet the needs of end-users, QA measures including sampling, sample treatment, analytical method, choice of quality parameters and data interpretation should be considered (Flamme and Geiping, 2014).

2.5.1 Sampling and sample preparation

The main operations during sampling are mixing, mass reduction (extract a small mass from a larger mass) and shredding (Petersen et al., 2005). Shredding and mixing are processes for sample homogenization (Petersen et al., 2005). The beneficial role of shredding in sampling is double: material homogenization creating more uniform and equal probabilities of all particles to be included in the sample; and liberation of analyte which otherwise might be occluded in large particles making difficult to detect it during analysis (Gy, 2012).

For the quality characterization of commercially produced SRF, samples are typically collected from the lot – the collective body of material under investigation to be represented – in a MT/MBT plant and delegated to the laboratory for analysis. The first step is the sample obtainment from the MT/MBT plant following the sampling protocol specified in the corresponding CEN/TC 343 standard (BS EN 15442, 2011). The typical mass of SRF sample received for analysis fluctuates between 0.8 and 159 kg depending on the grain size and bulk density, whereas the maximum mass of the lot can reach up to 1500 tonnes (BS EN 15442, 2011). Unless the total mass of the SRF sample as received in the laboratory can be directly analysed, laboratory sampling which is a repetition of sampling process – known as sub-sampling – is the next step following the CEN/TC 343 standard related to the sample preparation and sampling methods in the laboratory for SRF (BS EN 15443, 2011). During sub-sampling, the sample is split into sub-samples consecutive times to obtain the test sub-sample, which is ready for analysis (Prichard and Barwick, 2007). From the test sub-sample, a small mass is drawn for analysis, which is called the test portion (Prichard and Barwick, 2007). The test portion, with a mass ranging from milligrams to grams, must be sufficiently representative of the heterogeneous SRF lot based on the needs of the application area (Ramsey and Thompson, 2007).

Sub-sampling can be a major source of variability, which needs to be minimised in a way that maintains representativeness, minimises potential bias and enables precise quantification of material properties (Gerlach and Nocerino, 2003; Risso et al., 2012). The selection of sub-sampling techniques and shredding processes constitute the sub-sampling plan. The performance of a variety of sub-sampling techniques, such as riffle splitting, coning and quartering, fractional shovelling, etc. is described elsewhere (Gerlach and Nocerino, 2003; Gerlach et al., 2002). However, the role of sub-sampling of highly heterogeneous waste is poorly understood in the quantification of uncertainty of analytical measurements (Risso et al., 2012).

Sub-sampling consists of a series of laboratory operations, each of them can introduce a considerable uncertainty depending on the inherent material heterogeneity, sample preparation procedures (e.g. shredding processes), sample mass reduction practices, sub-sampling equipment, sensitivity detection of the analytical instrument, and skills of operator (Gerlach and Nocerino, 2003). Specifically,

incorrect practices induced during sub-sampling, such as human mistakes, loss of sample mass, contamination, chemical modification, physical and biological alteration of the sample (Edjabou et al., 2015; Pitard, 1993), may introduce bias increasing the uncertainty (Edjabou et al., 2015; Nocerino et al., 2005). Shredding can exceptionally induce such practices, despite the beneficial role it plays in the sampling process. For example, the heat generated during shredding may induce evaporation of a highly volatile analyte, such as mercury (Gerlach and Nocerino, 2003). Insufficient shredding may lead to: i) a systematic error during analytical determination; and ii) a wider range of particle size in the sample generating different probabilities of each particle to be included in the test sub-sample (Dominy et al., 2018a). Advanced sample preparation procedures such as cryogenic shredding should be considered. Cryogenic shredding is able to produce a fine particle size at very low temperature using liquid nitrogen preventing unwanted processes related to shredding (Junghare et al., 2017). Also, loss of mass can occur during sub-sampling due to either inappropriate handling of equipment, (e.g. use of riffle splitters by an unskilled operator) or equipment operation (e.g. dropping grains during shredding) (Gerlach and Nocerino, 2003).

There is a suggestion that sub-sampling uncertainty in the mining industry should be $< 15\%$ (Gerlach and Nocerino, 2003; Dominy et al., 2018b; Dominy et al., 2018a; Dominy et al., 2019), but the absence of relevant comparative evidence in characterisation of solid waste makes it difficult to have confidence in this value as acceptable limit. Sub-sampling can be designed and executed with a high level of control, with a view to minimise introduction of bias within reason of available resources (time and effort) (Gerlach and Nocerino, 2003). Despite that, design and implementation of optimal sub-sampling plans have received minimal attention to date (Gerlach and Nocerino, 2003; Cuperus et al., 2005). Previous studies focusing on sample preparation practices for the acquisition of representative analytical results of SRF exist (Schnöller et al., 2014; Cuperus et al., 2005; Robinson et al., 2016), but minimum evidence can be found for the entire sub-sampling scheme including sample preparation, mass reduction and analysis.

Pierre Gy's theory often referred to as 'Theory of Sampling' (ToS), which was developed mainly in the mining industry, provides what are widely regarded as the governing principles for representative

sampling (Pitard, 1993), which constitute the basis for the development of the related CEN/TC 343 standards on SRF sampling and sample preparation. During representative sampling, the obtained sample exhibits the average properties of the lot (Gy, 2012; Kratochvil and Taylor, 1981). ToS provides a mathematical formula that estimates the sampling uncertainty only due to the material constitutional heterogeneity (Pitard, 1993). This formula does not consider additional uncertainties related to analytical method, sample preparation and performance of sampling methods. Recently the ToS has been adjusted to sub-sampling of particulate materials by Gerlach and Nocerino (2003), who suggested practices and operations to minimize the uncertainty arising from sub-sampling process. The relevant theoretical approaches and practical recommendations benefiting from the ToS (Pitard, 1993) to test sub-sampling variations have received almost no attention. More details on the ToS are provided in **Section 2.5.1.3**.

2.5.1.1 Sub-sampling for determination of Cl

Total [Cl] in SRF is a critical technical factor with high variability (BS EN 15443, 2011) due to various chlorinated compounds present in waste items, such as plastics, textiles and food processing substances (**Table 2-9**). This condition in combination with SRF high inherent heterogeneity due to its origin (e.g. MSW (Cheng et al., 2017)), yet lower compared to MSW (Kallassy et al., 2008; Velis et al., 2010), features the importance of representative analytical results.

The measured [Cl] may vary considerably between samples. For example, Spurek (2012) determined the Total [Cl] in individual SRF samples delivered to a Polish cement facility: in 12 out of 70 samples, the Total [Cl] exceeded the recommended value. Total [Cl] in SRF should be kept at lower levels than recommended limit values considering the uncertainty arising from sampling and sub-sampling (Cuperus et al., 2005; Pitard, 1993). If this uncertainty is relatively high, then substitution rates of fossil fuels by SRF should be kept at conservative levels so that to prevent risks associated with unpredictable levels of Cl, a not resource – and cost-efficient decision (not optimal substitution rates).

The target particle size of an SRF test portion should be $\leq 1\text{ mm}$ for [Cl] determination (BS EN 15408, 2011). However, Cuperus et al. (2005) suggested a particle size $\leq 0.5\text{ mm}$ for 100% Cl recovery as insufficient shredding may lead to incomplete recovery of Cl during bomb calorimetry (BC) (Cuperus et al., 2005). Further research is required to investigate the impact of sampling process on the uncertainty of representativeness of [Cl] in SRF samples and assess the influence of analytical methods with Round Robin test.

2.5.1.2 Sub-sampling for TGA

In TGA of WDFs, the obtainment of representative analytical results is a major challenge due to the tiny amount of test portion required in TGA experiments. Specifically, the test portion subjected to TGA should be ranged on milligram scale at around 10-100 mg, so that to ensure uniform thermal conditions (Heal, 2002). The selection of a larger test portion for TGA would require considerably more energy and be more difficult to be placed in the thermo-balance (Robinson et al., 2016). Therefore, major attention should be paid on the sub-sampling process before TGA (Robinson et al., 2016).

Before TGA, samples should be pulverized to fine powders, whilst ideally avoiding the evaporation of volatiles (e.g. mercury or moisture), melting of fragments with low melting points (e.g. polyolefins (Pedersen et al., 2016)) and other related processes induced by the heat generated during pulverization (Gerlach and Nocerino, 2003). Robinson et al. (2016) examined the influence of sample preparation of RDF on the repeatability of TGA results. Several RDF samples were prepared by using a variety of equipment and procedures, such as knife milling, rotary grinding and cryogenic milling, finding that cryogenic grinding provided repeatable results. The particle size of the test SRF/RDF sample defined by the cumulative passing of sieve must be typically less than 0.25 mm to obtain uniform thermal behaviour throughout the sample body (Beckmann et al., 2012; Robinson et al., 2016).

2.5.1.3 Theory of Sampling (ToS): a potential tool of SRF/RDF sub-sampling

ToS addresses the factors that can induce sampling uncertainty and provides practices for its minimization. The notion of correct sampling based on ToS is that “*all fragments in the lot (the entire*

body from which a sample is drawn) must end up in the final sample with identical and nonzero probability” (Pitard, 1993). A correct sampling practice based on TOS gives each fragment of the lot an equal and constant probability of being selected from the lot to be part of the sample, aiming to create a composite sample (Pitard, 1993). Based on ToS, the sample mass should be obtained only through composite sampling creating a sample composed of individual material segments (Horn et al., 2018). Horn et al. (2018), compared the representativeness of grab sampling (non-representative) with composite sampling based on ToS (fit-for-purpose representative) for the characterization of biomass fuels, concluding that grab sampling gave inadequate representativeness and the number of individual segments may lead to a representative composite sample of the lot.

Herein, there are some main definitions that need to be reported to follow the principles of ToS (Gerlach and Nocerino, 2003; Pitard, 1993):

- Sampling is the action in which a small mass is drawn by a larger mass in order to analyze the smaller mass on specific parameters: the error induced by the sampling process is defined as sampling error (SE);
- Preparation is a sequence of actions, such as gridding, crashing, transfer, drying, that are used in order to bring the sample in a convenient form for the next stage (e.g. sampling or analysis): the error induced by the preparation process including contamination, mass loss, human mistakes and chemical and/or physical alterations is defined as preparation error (PE);
- Analysis is a procedure for the determination of a content of a constituent under of interest: the cumulative error associated with each stage of analytical method is defined as analytical error (AE);
- Lot is the collective body of material under investigation to be represented; e.g., a batch, a population, or populations. It is usually too difficult to analyse an entire lot, so a sample (a portion) is taken from the lot in order to make estimations about the characteristics of that lot;
- Analyte is the critical component of interest and a_L is the decimal proportion of the analyte in the sample.

Based on ToS, the variance of the overall estimation error of sampling is equal to the sum of the variances of SE, PE, and AE (Pitard, 1993):

$$S_{OE}^2 = S_{SE}^2 + S_{PE}^2 + S_{AE}^2 \quad \text{Eq. 2-2}$$

When a sample is characterized by high heterogeneity, such as SRF, the SE could overshadow the AE (Cuperus et al., 2005). Specifically, SE consists of five errors which are classified into correct (CSE) and incorrect (ISE) SE. Wagner and Esbensen (2015) described the relationship of these errors in stationary lot sampling, mentioning that ISE, which includes Delimitation Error (DE), Extraction Error (EE) and Preparation Error (PE), must be eliminated in any sampling scheme and originate from faulty or ill-informed sampling processes. On the other hand, CSE, which includes Grouping Segregation Error (GSE) and Fundamental Error (FE), constitutes the minimum SE and originates from the constitutional heterogeneity of materials. Although, CSE, ISE and AE (the sum is called overall sampling error) are insolubly connected during sampling process, FE is the only type of error that can be calculated before sampling takes place, as it is based on the physical and chemical properties of the sample (Gerlach and Nocerino, 2003).

Specifically, ToS developed a theoretical model for the prediction of the sampling uncertainty resulting from FE (Gy, 2012). Fundamental error is the minimum sampling uncertainty that is attributed only to the physical and chemical constitutional heterogeneity of the sample, other factors related to sample preparation, sampling method and chemical analysis that may introduce additional uncertainty are not included (Pitard, 1993). Based on this ToS-based formula, the FE is inversely proportional to sample mass and proportional to the cube of particle size of the sample (Pitard, 1993):

$$s_{FE}^2 = \left(\frac{1}{M_s} - \frac{1}{M_L} \right) C d^3 \quad \text{Eq. 2-3}$$

where M_s is the sample mass [g], M_L is the mass of the lot [g]; C is the sampling constant [g cm^{-3}]; and d is the nominal size of the particles [cm].

This formula could, also, be used in sub-sampling either for the calculation of minimum sub-sampling uncertainty (FE) for a given sample size or for the calculation of the required sample mass to obtain a specified FE (Dominy et al., 2019). At each stage of sub-sampling, M_s is the mass of the sub-sample

at this stage and M_L is the mass of sample or higher level of sub-sample (Gerlach and Nocerino, 2003). The square root of s_{FE}^2 gives the relative deviation of the FE expressed as (%). Every stage of mass splitting introduces FE, the summation of which gives the overall FE of the sub-sampling process.

Sampling constant, C , is the product of four factors related to the characteristics of the sample:

$$C = cflg \quad \text{Eq. 2-4}$$

where c is the mineralogical (or composition) factor [g cm^{-3}]; l is the dimensionless liberation factor; f is the dimensionless shape factor; and g is the dimensionless particle size range (or granulometric) factor. The physical characteristics of a sample change after shredding and therefore the values of these factors (BS EN 15442, 2011).

The mineralogical factor, c , is defined as follows:

$$c = \lambda_M \frac{(1 - a_L)^2}{a_L} + \lambda_g(1 - a_L) \quad \text{Eq. 2-5}$$

where a_L is the concentration of the critical component in the sample expressed as decimal proportion (e.g Total [Cl]); λ_M is the density of particles containing the critical component (e.g. plastic, textile or food materials that contain Cl) [g cm^{-3}]; and λ_g is the density of the sample (e.g SRF) [g cm^{-3}].

The liberation factor (l) ranges between 0 and 1 depending on the degree of heterogeneity. The more homogeneous the sample, the lower the l value. The shape factor (f) ranges between 0 and 1 depending on closeness of particle's shape to a perfect cube (where $f = 1.0$). The granulometric factor (g) accounts for the particle size distribution (PSD) by adjusting the particle sizes to a nominal value. The more uniform the particles, the higher the g value. According to BS EN 15442 (2011), the g factor should be kept at 0.25 for PSD $d_{95}/d_{05} > 4$. It should be noted that the precise quantification of these factors is difficult as a significant amount of information is required for the target material (Ramsey and Thompson, 2007). Estimation of theoretical uncertainty due to sub-sampling can be calculated and depicted as nomographs, enabling the design of optimal sub-sampling plans, associated with a targeted level of tolerable uncertainty (Gerlach and Nocerino, 2003). However, ToS has been

developed mainly in field sampling, while there is little evidence that this theory is verified not only on the experimental stage (Gerlach and Nocerino, 2003) but also on waste-derived materials that have different physical and chemical properties from granular materials.

2.5.2 Analytical chemistry

QA measures in the stage of analysis includes laboratory staff training, record keeping, appropriate laboratory environment, adequate storage facilities, documentation methods, and maintenance and calibration schedules (Prichard and Barwick, 2007). Technical issues of QA are related to: the equipment and reagents need for the selected analytical method; calibration of analytical method following quality standards and using reference materials and standard solutions; and validation of analytical method including several interrelated performance characteristics (e.g. sensitivity/calibration, limit of detection (LoD), precision, repeatability, bias/recovery, accuracy/uncertainty, selectivity, linearity, and ruggedness testing) (Prichard and Barwick, 2007; Barwick, 2016). These critical indicators used in validation can be used to assess the suitability of the analytical method for its particular needs (fitness-for-purpose) (Barwick, 2016), briefly described in **Table 2-11**. Further information can be found elsewhere (Barwick, 2016; Prichard and Barwick, 2007) .

Table 2-11. Definition of critical indicators used for the validation of analytical methods contributing to the assessment of QA in the stage of chemical analysis. Adapted by (Prichard and Barwick, 2007).

Factors	Definition	Mathematical formula	Actions
Selectivity	The extent to which a method can determine particular analytes in mixtures or matrices without interferences from other components.		Use of reference materials.
Precision	Standard deviation of the test results from repeat measurements, with repeatability and reproducibility being the two extreme conditions.	s_r : standard deviation of replicate measurements.	Increase the number of replicate measurements (acceptable levels depend on the levels of concentration).
Bias/Recovery	Difference between the mean value ($\bar{x}$) and an accepted reference value x_0 .	$\%B = \left(\frac{\bar{x} - x_0}{x_0} \right) \times 100$ $\%R = \left(\frac{\bar{x}}{x_0} \right) \times 100$	At least 7 replications of reference materials is required for the determination of bias

Factors	Definition	Mathematical formula	Actions
	Attributed to blank signals, non-linearity, incomplete recovery, matrix effects and potential interfering substance.		(preferable certified reference materials (CRM))
Linearity	A measure of a method's ability to give a response directly proportional to the concentration of analyte. Assessed by visual inspection of a plot of measured responses against standard concentrations.		Use of pure materials and CRM or spiked samples. A concentration range that is greater than the expected range for samples $\pm 20\%$ is needed.
LoD	The smallest amount of the analyte that the instrument can detect.	$LoD = 3s_{bl}$ s_{bl} : standard deviation of the blank signal/measures	
Ruggedness testing	Evaluates how small changes in the conditions affect the measurement result		
Calibration	The relationship between instrument response and corresponding values of a standard substance. The slope of the calibration curve expresses the sensitivity (the greater the sensitivity the better the method).		Use of reference materials (correlation coefficient close to 1, r^2) Measurement values should not extrapolate the concentration range of calibration graph!
Uncertainty	The closeness of the agreement between the measured and the true/ actual value. The effect of both precision and bias is included.	$\%U = x_i - x_o$ or $U = r + B$	Use of replicate measurements and determine the bias.

2.5.2.1 Focus on TG-DTG for compositional analysis

The experimental conditions applied in TGA, of which most important are heating rate, atmospheric conditions, and maximum temperature, affect the thermal behaviour of the sample and should be consciously selected (Haines, 2002; Bottom, 2008). The selection of experimental conditions depends on sample characteristics, such as particle size, calorific content, inorganic content, impurities, and chemical composition (Heal, 2002).

Heating rate affects the range of decomposition temperature of the sample (Marsh et al., 2007; Yurdakul and Atimtay, 2015; Słopiecka et al., 2012; Park et al., 2012; Wang et al., 2020). Increased heating rates result in higher decomposition temperatures and higher rates of mass loss and therefore

shifting the TG-DTG thermogram to the right (Conesa and Rey, 2015; Lin et al., 1999; Park et al., 2012; Quan et al., 2016; Yang et al., 2001; Yurdakul and Atimtay, 2015). By increasing the heating rate, the temperature gradient between the surface and inner of sample particles becomes larger which affects the total weight loss and the reactions forming volatiles (Quan et al., 2016). High heating rates can lead to significant overlapping effects between the heating profiles of the components contained in the sample resulting in interpretation problems of the results, e.g. in a mixture of plastics that contains polymers with similar ranges of decomposition temperature (Marsh et al., 2007; Bottom, 2008; Luo et al., 2018). But, too low heating rates are time consuming (Bottom, 2008; Heal, 2002). Heating rate can, also, affect the yields of products during thermal treatment. For example, Efika et al. (2015) found that increasing heating rates during pyrolysis induced higher gas yields and reduced liquid and solid yields. In TGA experiments conducted for compositional analysis purposes of waste-derived materials, the heating rate should be relatively low so that the peaks of DTG curves of waste components can be as discernible as possible (Beckmann et al., 2012).

The gaseous atmospheric conditions used in the TGA experiment is a crucial factor that affects the type of thermal process: e.g. combustion occurs in the presence of (over)stoichiometric oxygen, whereas pyrolysis occurs in the presence of inert, non-oxidising atmosphere, resulting in different thermal decomposition profiles of the sample and product formation (Conesa and Rey, 2015; Bottom, 2008). The presence of oxygen increases the rate of mass loss, and therefore reduces the range of decomposition temperature (Grammelis et al., 2009; Skodras et al., 2009). Specifically, Conesa and Rey (2015) reported that SRF is thermally decomposed in a range at nearly 50 °C lower during combustion compared to pyrolysis.

The maximum temperature applied in a TGA experiment might not be sufficient to ascertain the sample degradation (maximum temperature $\geq T_e$). It should suffice at least for the main stages of sample decomposition (inclusion of DTG peaks).

2.5.2.2 *Focus on determination of Cl content*

During analytical determination, several methods are available for the quantification of Total [Cl]. This include: bomb calorimetry (BC) combined with ion chromatography (IC) – the European standardized method for determination of Total [Cl] in SRF (BS EN 15408, 2011); quartz furnace methods; non-destructive methods, such as X-ray fluorescence; acid-destructive methods, such as inductive coupled plasma (ICP) technology; automated systems for elemental analysis (Ma and Rotter, 2008); and the Eschka method that can be applied directly in solid fuels (Rahim et al., 2014). The test portion varies over the range 0.05-100g depending on the analytical method.

Ma et al. (2010) compared five analytical methods for [Cl] determination BC, Schoeniger flask method (SFC), elemental analyzer (EA), elution test and muffle furnace by measuring the [Cl] on 8 fractions of residual household waste. The SFC method illustrated higher Total [Cl] compared with other methods, while BC presented less [Cl] due to potential incomplete combustion in the bomb or Cl loss during bomb ventilation (Ma et al., 2010). In addition, Österlund et al. (2009) reported that a sample preparation method based on sintering, followed by inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) analysis could be suitable in plastics and waste mixtures for [Cl] determination.

Despite the standard offline measurements conducted by laboratory analysis, there are online monitoring systems of HCl emissions produced during co-combustion, widely applied in cement plants or WtE boilers. These continuous monitoring systems are based on FTIR, gas filter correction, tunable diode laser and cavity ring-down technology (ICAC, 2013). Online measurements can offer sufficient control of HCl emissions during co-combustion and give a better understanding of measures to minimize these emissions by improving the operating conditions. In addition, online methods for monitoring of other chlorinated compounds in flue gas, such as dioxins and their precursors, have been investigated (Kuribayashi et al., 2005; Liu et al., 2016; Nakui et al., 2011; Gullett et al., 2011).

For a uniform kiln operation, the main properties of WDFs have to be monitored on a continuous basis (Bolwerk, 2004). So far, continuous monitoring systems are only available of chlorinated compounds in the flue gas (e.g. at the stack of the kilns). However, an online measurement system of

Total [Cl] in the input waste based on Eschka method synchronized with the moving conveyor belt or the alternative transport system before burning would lead to considerably better SRF QA.

2.5.3 Statistics

The selection and validity of statistical tools for the description of SRF properties has been described by Velis et al. (2010). The use of statistical tools for estimates of uncertainty, central tendency (e.g. mean, median, geometric mean), spread of values (e.g. standard deviation, median absolute deviation, coefficient of variation), and upper/lower limits of WDFs properties would give a more accurate knowledge compared to the determination of properties as single values which might be misleading (Velis et al., 2010; Chen et al., 2016).

The CEN/TC 343 rules for SRF classification indicate that NCV and Total [Cl] can be classified by the mean and confidence interval around the mean implying normal distribution, whereas mercury is classified by the median and 80th percentile indicating a skewed, long-tailed distribution (Velis et al., 2010). Despite the preoccupation of the CEN/TC 343 standards for sampling and sample preparation procedures for SRF characterization, the measurement uncertainty is not considered, only data on repeatability (a measure of precision and not uncertainty) of SRF properties are provided instead (BS EN 15443, 2011).

Uncertainty is defined as a quantitative estimate of the limits within which the analytically measured value is expected to lie (Barwick, 2016). For comparative purposes, the uncertainty is usually expressed as scale-free spread of values (e.g. coefficient of variation) (Gerlach and Nocerino, 2003). Note that repeatability or reproducibility, widely used for the quantification of the uncertainty (Cuperus et al., 2005; Robinson et al., 2016), are mostly estimates of precision rather than of uncertainty, since systematic errors (bias) related to analysis and sampling are not fully taken into account (Barwick, 2016). Compliance with quality management specifications necessitates the inclusion of the uncertainty along with the analytically estimated value (Velis et al., 2010). The exact deviation of a single measurement from the true, always unknown, value is impossible, but the likely range of deviation can be estimated (CITAC, 2002). Guiding principles and up-to-date description on

measurement uncertainty is provided by a Eurachem/CITAC publication indicating that the explicit consideration of possible sources of the uncertainty and evaluation of significant components are essential in the compliance evaluation (Barwick, 2016).

2.6 Summary of literature review

The European Commission has considered SRF utilization in co-combustion applications, mainly in cement industry, as an energy-efficient WtE technology compatible with the circular economy (European Commission, 2017). However, the inherent heterogeneity of SRF is the main limiting factor for a sustainable waste recovery system closing the loop of product lifestyles (Esbensen and Velis, 2016; EERE, 2019). A basic prerequisite for a wider uptake is a predefined and most importantly stable SRF quality (Flamme and Geiping, 2014). To achieve this, the introduction of QA measures are necessary providing a wider confidence on SRF uptake (Velis et al., 2010; Flamme and Geiping, 2014).

2.6.1 Product quality: end-user requirements

The high inherent heterogeneity of SRF feedstock (e.g. MSW) leads to a variable and therefore unpredicted thermal behaviour during co-combustion resulting in difficulty for the operators to adjust thermal recovery processes around a tightly defined Cl level (Beckmann et al., 2012). The variability of SRF thermal behaviour (Hilber et al., 2007b) and Cl content (Pomberger and Sarc, 2014) constitute maybe the most critical factors for industrial off-takers, with cement industry being the primary end-user (Theulen, 2015; Samolada and Zabaniotou, 2014).

SRF is a complex mixture of components at multiple levels including an assembly of waste items, materials and chemical compounds. The identification of the most prevalent components at multiple levels can offer valuable insights. Dominant polymers in SRF/RDF are biopolymers including cellulose, hemicellulose and lignin (biomass) which can be found in biomass waste item categories (*paper/cardboard*, *wood*, *non-wood biomass* for papermaking and *natural fibres*) and fossil-based plastic polymers including PE, PP, PET and PVC (plastics). Polyolefins and PET mainly represent

plastic packaging and synthetic fibres, respectively, whereas PVC represents the Cl content in simulated SRF/RDF samples. Xylan found to be the most commonly used substitute for hemicellulose in thermal analysis of waste-derived materials.

Although TGA is one of the most widespread thermal analytical techniques, it is far from a standardised technique regarding assuring quality of SRF/RDF. However, many researchers investigated SRF/RDF thermal behaviour through TG-DTG (**Table 2-5**). Specifically, TG-DTG thermogram of SRF/RDF typically consists of two peaks arising from the degradation of biomass and plastic materials (Danas and Liodakis, 2018) in a temperature range of 200-600 °C (**Table 2-5**). The thermal stability of polymers depends on their macromolecular structure. Biopolymers present a more variable thermal behaviour than plastic polymers due to the variety of natural sources (e.g. wood species) and/or the extraction method (e.g. type of pulping). Lignin is the most heterogeneous biopolymer, whereas cellulose is the most homogeneous. However, the presence of additives in post-consumer plastic materials can considerably change the properties and consequently the thermal stability of plastic materials in SRF/RDF (Sabet et al., 2019). Fossil-based plastic polymers have quite similar decomposition profiles, except for PVC (**Table 2-7**). Cellulose thermogram is similar to hemicellulose (xylan), whereas lignin has a completely differentiated thermal behaviour (**Table 2-6**).

Differences between the thermal behaviour of synthetic (simulated) and genuine waste samples exist due to cross-contamination, the potential presence of interaction effects amongst waste components and the presence of other unknown substances at low concentrations (e.g. extractives, additives, adhesives) (Grammelis et al., 2009; Cuperus et al., 2005). This aspect should be carefully considered when SRF composition is simulated for identification purposes.

The main limitations of TG-DTG used for compositional analysis is the presence of considerable overlapping degradation areas amongst the individual waste components and the uncertainty on the existence of interaction effects. However, simulation of TG-DTG thermograms of SRF/RDF by statistically designed experiments along with applications of artificial intelligence can lead TG-DTG to a strong tool for composition identification of waste-derived materials.

Cl content in SRF is widely dispersed amongst various items present in MSW, and is present in many chemical forms. Specifically, various forms of organically bound Cl (e.g. PVdC, EPI, DCM, TCE and phosgene) and inorganically bound Cl (e.g. NaCl, KCl and CaCl_2) could constitute considerable sources due to their wide application in packaging, textile and food industry materials (**Table 2-9**). This information could enable differentiation of sorting strategies during mechanical processing of MSW to produce an SRF which is low in Cl, going beyond the current preoccupation with identifying and/or removing only PVC.

Cl circulation may affect the clinker manufacturing process and cause operating problems in the kiln, such as build-up and ring formation, corrosion and clinker quality degradation (Cortada Mut et al., 2015; Karstensen, 2006). The recommended Total [Cl] in SRF, as applied in fact by the cement industry, is nearly 1% w/w_d, but it depends on the requirements and configuration of the cement plant (with a typical range reported of 0.5-2% w/w). Chlorine-related problems during SRF pre- and co-processing can be controlled (**Table 2-8**).

2.6.2 Post-production QA measures

The adoption of a QMS ensures that SRF characterization was carried out under a control manner following a documented validated method (Barwick, 2016). Special attention should be paid to single QA aspects including sampling, chemical analysis and statistical descriptors (Velis et al., 2010).

Adherence to a strict sampling protocol, including both field (sampling in MT/MBT plant) and laboratory sampling (sub-sampling), is a prerequisite for keeping the uncertainty at reasonable levels, especially in solid waste characterisation (Prichard and Barwick, 2007). The uncertainty associated with the sampling can exceed the uncertainty associated with the analytical method by an order of magnitude or more in heterogeneous materials, such as WDF (Gerlach and Nocerino, 2003).

Despite the preoccupation of researchers and industry with the variability of SRF properties (Cuperus et al., 2005; Velis et al., 2010; Deans et al., 2016), the uncertainty arising from sampling and sub-sampling processes has not been quantitatively determined yet. This can be achieved by implementing the design of experiment (DoE) approach using theoretical, practical and statistical tools that could

capture and describe the variability (Esbensen and Velis, 2016). If quantified evidence on the effectiveness of sampling practices existed, optimal cost-effective sampling approaches could be suggested and adopted (Dominy et al., 2018a; Dominy et al., 2018b).

Guiding principles on representative sampling along with a mathematical formula for the quantification of sampling uncertainty – only due to the material constitutional heterogeneity (FE) – are provided by the ToS (Pitard, 1993). This formula has been adjusted to sub-sampling by Gerlach and Nocerino (2003) to provide the theoretically minimum uncertainty at each stage of sub-sampling (nomographs) enabling the design of a fitness-for-purpose sub-sampling plan (Gerlach and Nocerino, 2003). However, ToS has been developed mainly in the field sampling, while there is little evidence that this theory is verified on the experimental stage (sub-sampling), especially in waste-derived materials (Gerlach and Nocerino, 2003). Special attention should be paid to sub-sampling for determination of Total [Cl] in SRF, a critical technical property with relatively high variability (BS EN 15443, 2011), and for TGA, a technique that requires a tiny amount of test portion (Heal, 2002).

Technical issues of QA in the stage of analysis focusing on Total [Cl] determination and TGA of SRF were also described. In TGA, attention should be paid to heating rate, atmospheric conditions, sample mass, and maximum temperature (Haines, 2002; Bottom, 2008). In Total [Cl] determination, evidence indicated that the standardized method (BC-IC) (BS EN 15408, 2011) tends to underestimate Total [Cl] (Ma et al., 2010) indicating the need to consider the systematic error arising from the stages of analysis.

The selection of valid statistical tools for interpretation of analytical results is also a necessary QA measure for SRF product quality. Compliance with quality management specifications necessitates the inclusion of the uncertainty along with the analytically estimated value (Velis et al., 2010).

3 AIM AND OBJECTIVES

3.1 Research gaps

In the literature review, a number of research gaps related to post-production quality assurance of SRF, were identified:

- Limited understanding on the heterogeneous composition of waste-derived SRF and how this can affect the thermal behaviour of SRF including potential thermal overlap and interaction effects;
- No current model able to identify the composition of SRF providing information on its properties and therefore assuring its quality before use;
- No standardized or either sufficiently developed techniques for the determination of thermal behaviour of SRF, such as TGA which is one of the most widespread thermal analytical techniques;
- Limited attention to the fate of Cl during SRF co-combustion in cement kilns;
- Limited attention to other considerable sources of Cl apart from PVC by SRF manufactures (MT/MBT plants);
- No data on the suitability of ToS in sub-sampling of waste-derived materials;
- Minimal attention to design and implementation of optimal (fitness-for-purpose) sampling and sub-sampling plans including sample preparation and analysis;
- No or very limited data on the uncertainty emerging from sampling and sub-sampling that can considerably affect the representativeness of analytical results, for all solid waste materials, SRF included;
- Absence of comparative evidence on an acceptable sampling and sub-sampling uncertainty for the characterization of waste-derived materials.

Here I have selected to investigate in depth a series of important and interconnected research gaps from the list above, in a coherent body of research, as manifested below in the overall research aim and specific research objectives.

3.2 Aim

The overarching aim of the research I conducted was to establish a novel toolkit for SRF characterization suitable for post-production quality assurance, including a predictive model for composition identification coupled with optimal practicably actionable (fitness-for-purpose) sub-sampling plan ensuring maximum accuracy and uncertainty minimization.

3.3 Objectives

The aim of the research has been achieved by executing a series of research objectives. Specifically, the objectives of this PhD are the following (**Figure 3-1**):

- **O1:** To review and critically assess the challenges around CI arising from both stages of SRF pre-processing and co-processing, as the key limiting factor for wider use and higher uptake of SRF in modern cement kilns (cyclone preheater/precalciner kilns);
- **O2:** To establish a fitness for purpose sub-sampling plan for SRF characterization using affordable and straightforward sub-sampling practices and current state of the art equipment by assessing different sample preparation scenarios with the use of the ToS formula;
- **O3:** To empirically quantify the overall uncertainty arising from the established sub-sampling plan for the determination of key SRF properties and compare the results with the theoretical ToS calculations in order to assess the suitability of ToS in sub-sampling of waste-derived materials;
- **O4:** To invent and validate a model predictive tool for composition identification of SRF based on its prevalent components predicated on thermal and spectroscopic analytical techniques.

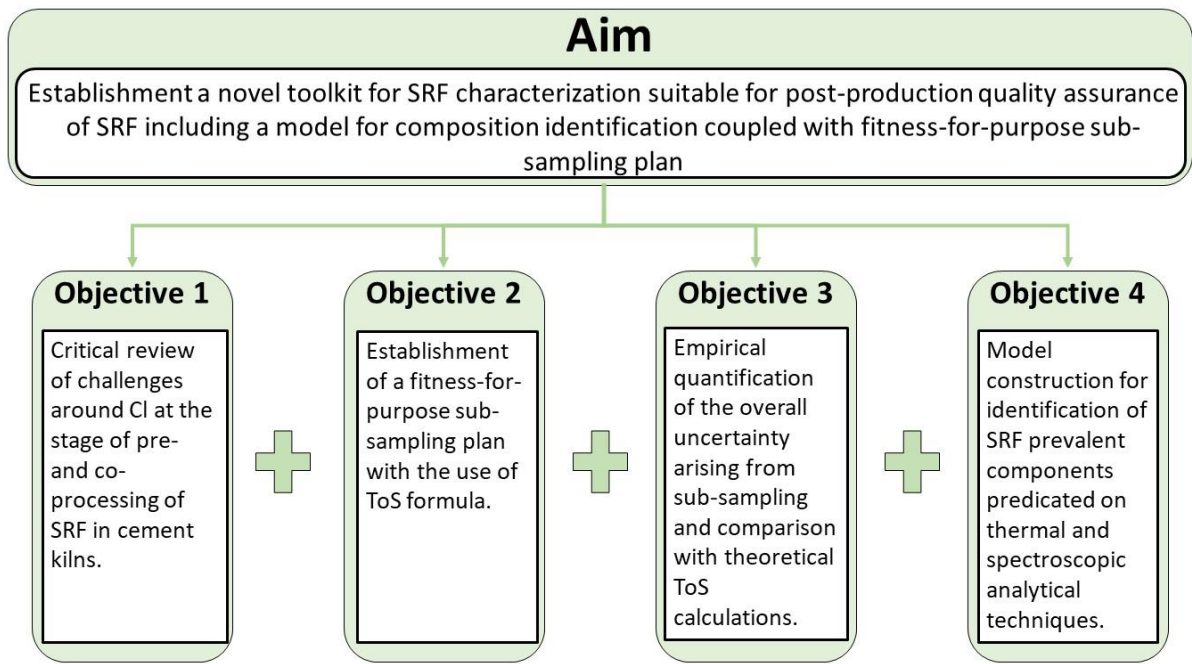


Figure 3-1. Overarching research aim and objectives of research, addressing a coherent suite and research gaps identified in the systematic literature review.

Herein, it is explained how the research objectives interlink to reach the aim of the Thesis. Literature review stressed the urgent need to set QA measures and practices able to deliver a stable and predefined SRF quality (Velis et al., 2010; Flamme and Geiping, 2014) in order to facilitate the transition towards circular economy (Esbensen and Velis, 2016). From that perspective, the present research aims to provide a practical and adaptable QA toolkit in SRF sector delivering major advances towards assuring SRF quality, and therefore increasing its marketability.

The predictive model for SRF composition identification at polymer level is an analytical-based tool that can provide a substantially better understanding of SRF composition and potentially its composition-dependant properties (**O4**), for both SRF producers (post-production) and end-users (pre-recovery). For any such analytical determination-based tools to be of practical use, especially if aiming to characterise highly heterogeneous mixes is the case with MSW-derived outputs, confidence is needed in the sub-sampling and wider sample preparation in the laboratory (e.g. establishing representativeness, controlling uncertainty). The review of the literature evidenced indicated the importance of laboratory sampling practices on characterisation of such heterogeneous materials and the risk to obtain misleading results if no attention was paid to this perspective (**Section 2.5.1**) – but

also revealed critical gaps in current knowledge. Therefore, the quantification of uncertainty arising from laboratory sampling for SRF characterisation (**O3**) and adherence to a practicable sub-sampling plan with tolerable levels of uncertainty (**O2**) are two integrated objectives that need to be executed to ascertain the reliable applicability of the analytical-based predicted model (**O4**).

A special attention is paid to Cl, which is a key limiting factor for SRF end-users (**Section 2.4.3**). By assessing the current challenges of Cl when SRF applied in cement industry – the main SRF end-user – (**O1**) along with the knowledge on SRF quality that can be obtained from the novel toolkit (**O2, O3, O4**), tolerable levels of Cl variability could be customised throughout its resource recovery supply chain.

4 METHODOLOGY

The methodology of this research consists of three main parts: a critical systematic review (**Section 4.1**) and two different DoE (**Section 4.2 and 4.3**). Each methodological part consists of a series of work packages aiming to meet the research objectives in an interdependent manner. **Figure 4-1** presents an overview of methodological part including work packages which are explained in detail in the following sections.

Knowledge background on the methodological approaches of critical review and DoE is also given:

Critical systematic review was conducted following the principles of the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) approach. PRISMA is an evidence-based minimum set of items widely applied in systematic reviews and meta-analysis – quantitative analysis to assess the results of previous studies (Moher et al., 2010; PRISMA, 2020b). The PRISMA flow diagram, that depicts the flow of information through the different stages of systematic review, helps authors to improve the reporting of systematic reviews (Moher et al., 2010). PRISMA diagram outlines the number of records identified, included and excluded along with the related exclusion criteria (PRISMA, 2020a).

Design of experiments consist of a series of experiments combined with applied statistics to gain insights into the relationships between input and output variables in a cost effective and reproducible manner (Salmaso et al., 2019) leading to valid and objective conclusions (Montgomery, 2017). Experimental design and statistical analysis constitute the main parts of a DoE (Montgomery, 2017). A statistically designed experiment deals with planning, conducting, analysing and interpreting controlled tests to assess the effect of input variables on the responses (Oehlert, 2010). DoE is a multipurpose tool widely applied in industrial sector of several fields, such as pharmaceutical (Beg et al., 2019), agricultural (Singh and Masuku, 2012), engineering (Ilzarbe et al., 2008) and food processing (Granato and de Araújo Calado, 2014).

DoE consists of the following steps : i) pre-experimental planning including identification of the problem, selection of response variables and choice of factors, levels and ranges; ii) choice of experimental design; iii) experiment execution; iv) statistical analysis; and v) reporting conclusions and recommendations (Montgomery, 2017). There is a wide variety of experimental designs with the

most prevalent being factorial designs, nested designs, screening designs, response surface designs and mixture designs, which are explicitly described by (Oehlert, 2010). The three basic principles of experimental designs are: i) randomization indicating that the allocation of experimental materials and the order of experimental runs were performed randomly since statistical methods treat the observations as independently distributed random variables; ii) replication indicating independent repeat run of individual observations so that to gain insights into the experimental error and obtain precise estimates; and iii) blocking indicating a set of homogeneous experimental conditions so that to avoid any unwanted variations in the experimental process (Montgomery, 2017). Guiding principles on the establishment of experimental designs and implementation of related statistical tools can be found in in the literature (Oehlert, 2010; Brereton, 2007; Montgomery, 2017).

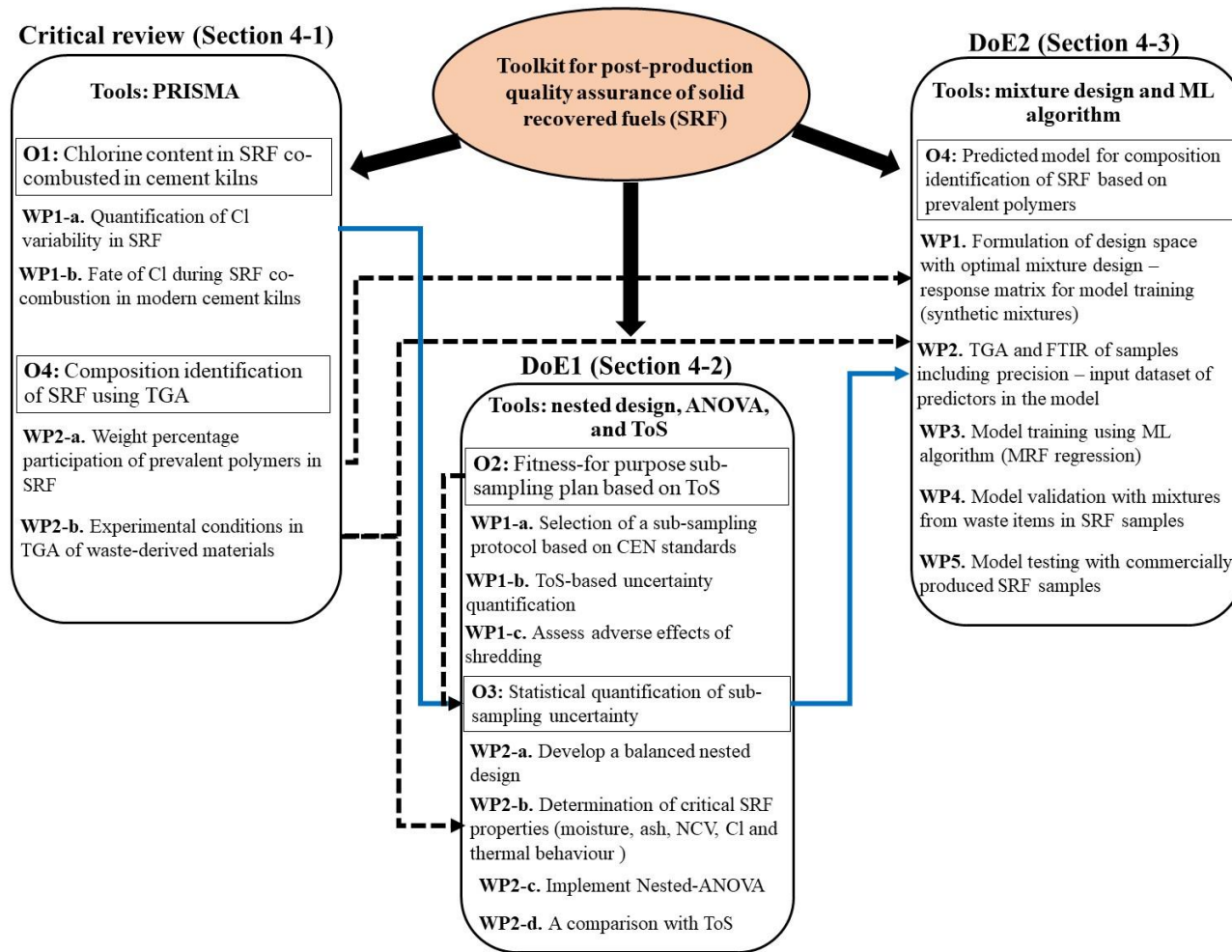


Figure 4-1. Overview of methodological parts for the overarching aim including work packages (**WP**) and research objectives (**O**) in an interrelated manner: dotted black lines indicate that the results from the related WP or research objective used to address the respective WP or research objective. Note: blue lines indicate that the results from the related WP or research objective were compared with the results from the respective WP or research objective; dotted black lines indicate that the outcome of the related WP or O was the basis on the conduction of the respective WP or O.

4.1 Critical review

This methodological part consists of two critical reviews following the PRISMA approach. The first part focuses on Cl content in SRF co-combusted in cement kilns to reach the first objective (**O1**) of this research. The second part focuses on the compositional analysis of SRF with the use of TG-DTG, which was the knowledge background for the design and experimentation related to the fourth objective (**O4**).

A PRISMA flow diagram was adopted, consisting of five key stages, including scoping, planning, searching, screening and eligibility, in line with Siddaway (2014). Specifically: in the stage of scoping, I identified the novelty of systematic review and formulated the research questions which synthesizes the review. The stage of planning included splitting of research questions into more specific ones, selection of scientific databases, and identification of key-words based on the literature findings. The stage of searching includes the introduction of keywords into the selected databases, inspection of search results, and record-keeping of all potentially relevant literature. In the stage of screening, the topic relevance of records was briefly examined by reading the title and abstract of the related scientific documents and duplicate records are removed. Finally, eligibility criteria and extraction of relevant information included in the systematic review are actions that carried out in the stage of eligibility (Siddaway, 2014). The completed PRISMA process resulted, in a final number of records included in the systematic review smaller than the initial number of records identified in the stage of searching, as anticipated (Moher et al., 2010). The PRISMA statement has been discussed in detail elsewhere (Moher et al., 2010; Knobloch et al., 2011; Panic et al., 2013).

4.1.1 O1: Challenges of Cl as a key limiting factor for SRF co-combustion in cement kilns

Herein, I assembled and compared the accurately known information, with a view to critically assess the challenges around Cl arising from both stages of pre-processing with a focus on Cl variability and co-processing with a focus on its fate during SRF co-combustion. The PRISMA approach ensures the empirical evidence has been systematically collated and critically analysed to address the two key

research questions: (RQ1) quantification of Total [Cl] in commercially produced SRF samples as reported basis and therefore assessment of Cl variability in SRF (pre-processing); and, (RQ2) the Cl distribution on cement production processes, when co-combusting SRF (co-processing).

Document types used in the scoping stage included: peer reviewed publications, industry reports, books, and PhD/ MSc theses. In the PRISMA planning stage, the two key RQs were split into specific sub-questions and search terms were selected covering materials, processing and operational conditions, as well as their combinations (**Table 4-1**). Scientific databases such as Scopus, Web of Science and Google Scholar were searched for the keywords. The topic relevance of studies was assessed during the screening PRISMA stage, and the assessment covered document title, abstract and conclusions.

Exclusion criteria were posed during the eligibility stage for both key research questions, which are described below. From the 743 documents identified as potentially relevant, only 55 were finally selected (ca 7%). Such exclusion criteria enabled existing actual research gaps to be identified, where reliable information was not available. The PRISMA flow diagram (**Figure 4-2**) presents the flow of information through the different phases of the systematic review.

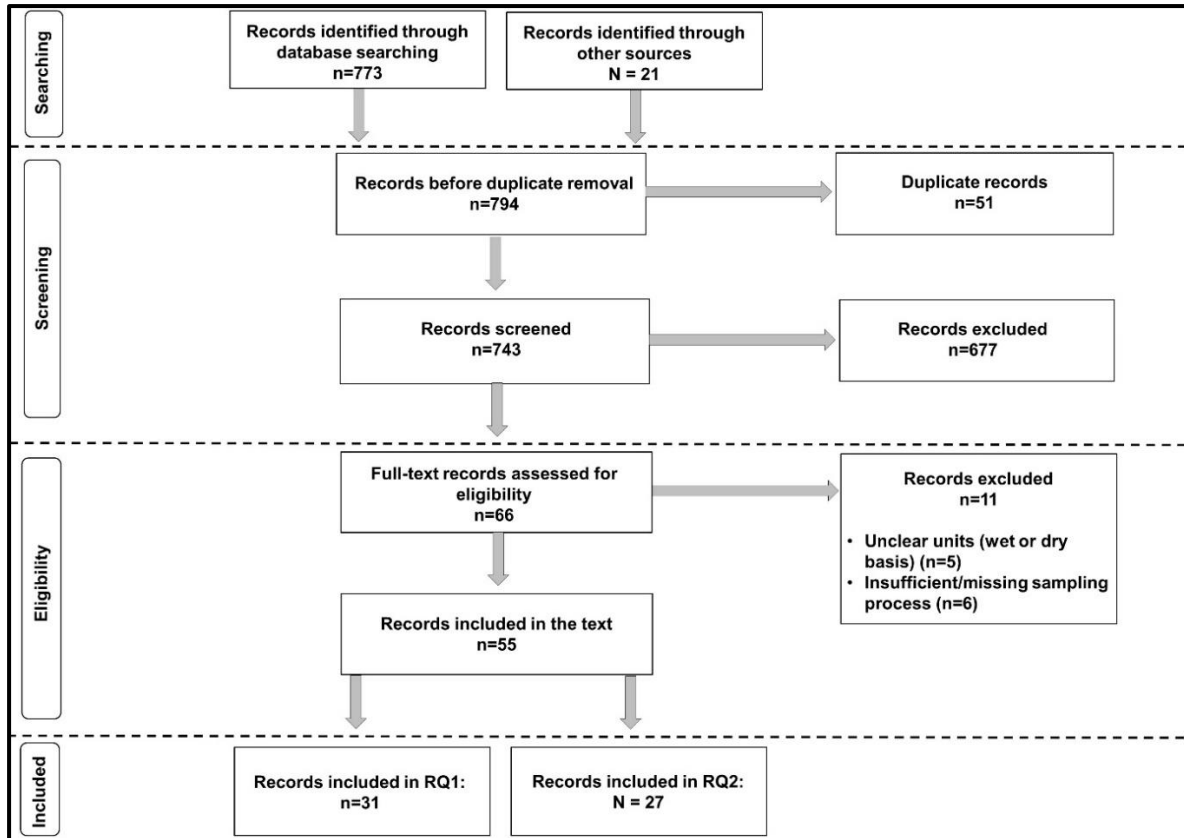


Figure 4-2. Flow of information through the different phases of systematic review (PRISMA flow diagram) for Cl in SRF co-combusted in cement kiln systems.

4.1.1.1 RQ1: Quantification of Cl variability in SRF

For the assessment of variability of Total [Cl] in SRF (RQ1), only studies that described adequately the analytical method for Cl determination, the sample preparation and sampling process of commercially produced SRF were included. Studies that did not clearly define whether the Cl was reported on wet or dry basis, and/or carried out sampling process deemed as insufficient (e.g. grab sampling) were excluded. Specifically, datasets on Total [Cl], in SRF, MSW and its constituting waste components were collected, classified based on the type of waste, and statistically analysed. Datasets were collected reporting the Total [Cl] from 9, 12 and 11 studies reporting the Total [Cl] as measured in MSW, SRF and different waste component categories, respectively.

Synthetic SRF samples (i.e. artificially constructed from individual components) have been used in past research to obtain insights into the fate of Cl in combustion processes (Cuperus et al., 2005; Wang et al., 2002; Yasuhara et al., 2001; Wagland et al., 2011), but were excluded here from the statistical analysis. The composition of synthetic SRF samples is not standardized (e.g. an SRF

component called ‘hard plastics’, may in fact contain considerably different combination of polymers in different studies), whereas NaCl and PVC were the exclusive or prevalent sources of Cl (**Table 2-4**). However, in commercially produced SRF, the Cl load may also stem from other major sources, such as synthetic rubber and food additives, which questions the accuracy of such simulations (**Table 2-9**).

The partitioning and terminology of waste components was inconsistent across studies. For example, the generic category of *plastics* in certain cases was split further into more specific categories, such as ‘packaging’ and ‘non-packaging’ or ‘soft’ and ‘hard’ plastics. Specific categories were grouped here into more generic groups for consistency and comparability, using just five prevalent waste fractions, namely *plastics*, *paper/cardboard*, *wood*, *textiles* and *rubber-leather*. Adjusted concentrations were obtained by multiplying the Total [Cl] in the specific item category with their proportion in the generic item category. The summation of these calculations gave the Total [Cl] of the generic item category (e.g. *plastics*). However, Total [Cl] can be expressed using different units: so normalization was performed to convert all estimates into % weight on a dry basis (% w/w_d) to enable comparisons. Basic descriptive statistics and graphic analyses were performed in TIBCO Statistica™ 13.3.0 software. The central location for the three sample populations (MSW, SRF and waste components categories) was determined (arithmetic mean and median) along with upper and lower 95% confidence intervals. Extent of relative variability was expressed as coefficient of variation (CV). It was assumed that all the selected cases (studies that measured [Cl]) were of equal importance, although the number of samples was different in each case, and these were reported where available.

4.1.1.2 RQ2: Fate of Cl during SRF co-combustion in modern cement kilns

In order to gain insights on the fate of Cl when SRF co-combusted in modern cement kilns (RQ2), limited exclusion criteria were applied, due to the confined literature. Cl behavior in a modern cement kiln – cyclone preheater/precalciner kilns – has been examined by the application of WDFs with high [Cl] and by the addition of Cl in raw meal, since Cl is mainly introduced to the kiln through the raw

materials and fuel (Saxena, 2003; Enders and Haeseli, 2011; Cortada Mut et al., 2015). Information was obtained to provide a generalised mass flow of typical Cl distribution during SRF co-combustion.

Table 4-1. Search terms and two main research questions systematically reviewed, according to PRISMA principles.

Search terms			
Materials	Compounds	Application	Fate of Cl
Solid recovered fuel	Chlorine	Cement plant	Clinker
Waste derived fuel	Chloride(s)	Cement kiln	Flue gas
Municipal solid waste	Hydrogen chloride	Suspension preheater	Cement kiln dust
Household waste	Chlorinated compounds	Precalciner kilns	Corrosion
Alternative fuel		Combustion	Operating problems
Main research questions (RQ1, RQ2), and specific sub-questions			
RQ1: Quantification of Cl variability in SRF		RQ2: Fate of Cl during SRF co-combustion in cement kilns	
What is the Total [Cl] in commercially produced SRF and its components?		How is the Cl content distributed during co-combustion in a cement kiln system?	
What is the Cl concentration in SRF with respect to criteria of Cl categorisation?		What are the main chloride compounds that can be found during combustion of SRF in a cement kiln?	

4.1.2 O4: Composition identification of SRF using TG-DTG

By ways of comprehensive literature review, I collated and critically comparatively assessed recent scientific developments to address two research questions: (RQ1) percentage participation of the most prevalent polymers in commercial SRF/RDF produced from MSW; and, (RQ2) determination of *non-isothermal* operating conditions usually applied in TG-DTG of SRF/RDF and its components for compositional analysis purposes.

Due to the lack of acknowledged guidelines for narrative reviews, the PRISMA methodology (Ferrari, 2015) adopted in systematic reviews (Selçuk, 2019) was applied. In the first stage of PRISMA, key words (RDF, SRF, MSW, plastic, biomass, biopolymer, cellulose, lignin, waste, TGA, DTG, composition, and thermal degradation), scientific databases (Scopus, Web of Science and Google

Scholar) and document types were identified, while the topic relevance of findings was assessed during the screening stage.

4.1.2.1 RQ1: Weight percentage participation of prevalent polymers in SRF

In regard to RQ1, I obtained studies that quantified the weight percentages only of prevalent polymers included in several MCP waste categories. Descriptive and inferential statistics (lower and upper confidence interval (LCI-UCI) at 0.1 significance level: $\alpha=0.1$) were visually summarised in boxplots (TIBCO Statistica™ 13.3.0 software), reporting on: i) the weight percentage of cellulose, hemicellulose and lignin content in several biomass waste MCP present in SRF/RDF expressed on dry basis (% w/w_d); and ii) the percentage participation of prevalent fossil-based plastic polymers in the plastic fraction of SRF/RDF (% w/w).

4.1.2.2 RQ2: Experimental conditions in TGA of waste-derived materials

In regard to RQ2, the main eligibility criterion was the inclusion of studies that conducted only *non-isothermal* TGA in prevalent post-consumer items/materials, plastic and biomass polymers, and SRF/RDF. The conditions applied to TGA experiments (heating rate, atmosphere, sample mass and maximum temperature) in several studies were analysed and graphically presented. The results of the selected heating rates were presented in terms of TGA experiments (not based on studies), because some researchers conducted more than one TGA experiment with different heating rates.

4.2 Design of experiment 1: sub-sampling plan and uncertainty quantification

This part of methodology consisted of two main steps: the establishment of a relatively unbiased, yet affordable and practicable sub-sampling plan (fitness-for-purpose) for the characterization of SRF (O2); and the quantification of uncertainty arising from the entire sub-sampling scheme including sample preparation, mass reduction and analysis for determination of critical quality properties of SRF (O3).

In the first step (**O2**), a sub-sampling protocol was applied using state of the art equipment and following the guiding principles of ToS along with general guidelines of the related CEN/TC 343 standards. During the selected sub-sampling process, incorrect sub-sampling practices were monitored that may introduce bias and therefore increase the sub-sampling uncertainty gaining insights into the adverse effects of shredding, as discussed in **Section 2.5.1**. The uncertainty arising from this protocol was theoretically estimated with the ToS formula (**Eq. 2-3**) and compared with different sample preparation scenarios. This comparison gave insights into the beneficial role of shredding resulting in the establishment of a sub-sampling protocol that fulfils the fitness for purpose requirements. The design of this protocol focused on the development of a straightforward and affordable sub-sampling process suitable for solid waste materials. The selected critical component was Cl as one of the most important technical parameter for SRF applications (BS EN 15359, 2011). This choice was a compromise between SRF properties with low and high variability amongst waste components, such as moisture content and mercury, respectively (BS EN 15442, 2011).

In the second step (**O3**), a statistically designed experiment was developed to simulate this established sub-sampling plan, in which multiple consecutive steps of sub-sampling and shredding took place for the obtainment and chemical analysis of test sub-samples. Following this sub-sampling plan, analysis of variance (ANOVA) for a balanced nested design approach was used for the quantification of: the overall uncertainty emerging from inherent material heterogeneity, sample preparation (e.g. shredding), sub-sampling practices (e.g. human mistakes and performance of riffle splitting), and analysis (systematic and random error); and, the relative contribution of each step of sub-sampling scheme to the overall uncertainty (as a ratio of the variance at each stage to overall variance). The sub-sampling uncertainty was quantified for the determination of critical SRF properties including moisture, ash, NCV, Cl and thermal behaviour (with the use of TG-DTG). This empirically measured sub-sampling uncertainty was compared and contrasted with the theoretical estimation of sub-sampling uncertainty as calculated following the ToS stipulations. **Figure 4-3** presents an overview of the steps that were followed to carry out DoE1.

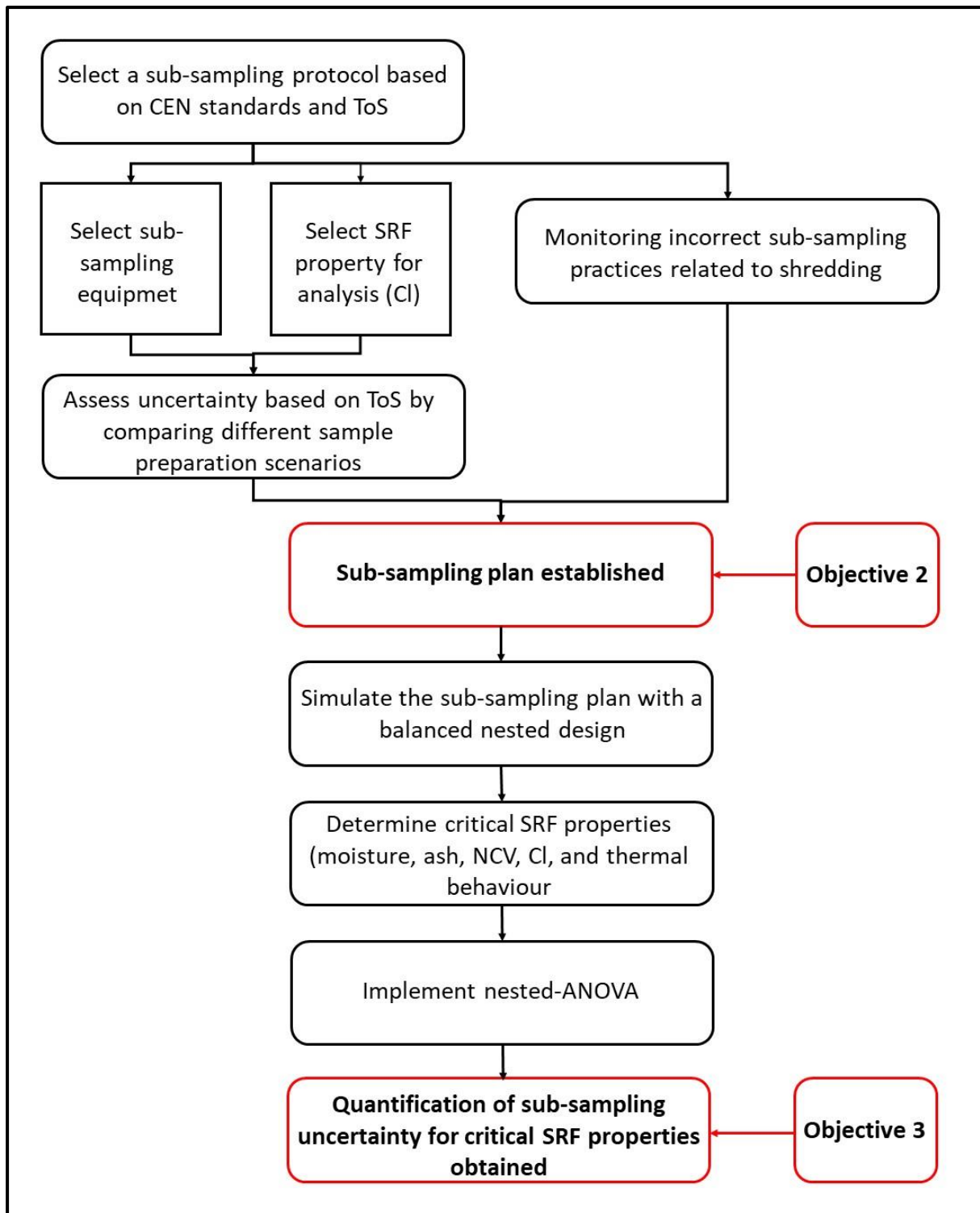


Figure 4-3. Methodological overview for DoE1 to address the research objectives (O2 & O3).

4.2.1 Materials of DoE1

A typical SRF sample (ca. 1kg) produced from residual MSW in a MT plant in the UK, processing a mixture of residual household MSW and commercial waste (corporate name withheld for confidentiality reasons), was obtained. The analytical technique for the determination of Total [Cl]

involved reagents, 0.2 M KOH (Sigma-Aldrich, UK) for Cl absorption during combustion in the bomb calorimeter, Palintest acidifying and silver nitrate tablets (Sigma-Aldrich, UK). Liquid nitrogen was used for the cryogenic shredding. Reference materials (Sigma-Aldrich, UK) were used to resemble SRF composition and calculate the recovery of Cl: powder microcrystalline cellulose, alkali lignin, xylan from beechwood, high density polyethylene (HDPE), isotactic polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC).

4.2.2 Sub-sampling protocol

The sub-sampling process consisted of two stages of shredding and multiple stages of mass splitting according to BS EN 15413 (2011) (**Figure 4-4**). The sub-sampling operations and equipment were applied as follows: The SRF sample was pre-dried at 40 °C for 24 h to remove the moisture that could interfere with the shredding process (BS EN 15414-3, 2011) (1). After pre-drying the sample mass was reduced at ca. 850 g. The pre-dried sample was spread on a canvas forming a thin layer (≤ 2 cm) and a magnet passed over the layer to pick any ferrous metals that could damage the shredders (2). The pre-dried sample with a particle size ca. 3 cm was divided into two sub-samples with large riffle splitters (RT 75, Retsch, Germany) (3). The sub-samples were shredded with cutting mill (SM 300, Retsch, Germany) to a particle size $d_{90} \leq 4$ mm (primary shredding) (4). The shredded sub-samples were divided with small riffle splitters (PFEUFFER GmbH, Germany) multiple times obtaining 16 sub-samples of ca. 50 g each (5). A test sub-sample of 7 g was drawn from each of the 16 sub-samples with riffle splitting and cryogenically shredded (Cryomill, Retsch, Germany) to $d_{90} \leq 150$ μ m (secondary shredding) (6). From these 16 test sub-samples of 7 g, three test portions were obtained for analytical determination of Total [Cl] (0.3 g) and moisture content (1 g) as specified by the related CEN/TC 343 standards (**Section 4.2.7.2**) (7).

Cutting mill was used as suitable for primary size reduction of highly heterogeneous materials, such as solid waste including soft, medium-hard, elastic and fibrous materials able to achieve a defined final fineness from the first shredding run (Retsch, 2020b). The process was conducted by the sample comminution between the blades and the stationary double acting cutting bars (Retsch, 2020b).

Cryomill was used as suitable for secondary cryogenic shredding (material feed size ≤ 8 mm)

producing a fine particle size under inert atmosphere at very low temperature (-196 °C) through an integrated autofill liquid nitrogen system. The main components of cryomill are a 50 ml steel grinding jar with screw-top lids, a 25 mm steel grinding ball, a cooling jacket, an integrated cooling system, and a display and control unit. The grinding jar is filled with the grinding ball and the sample material (SRF sub-samples after shredding with Cutting mill) at a level 70-80% of the grinding jar volume. The grinding jar is placed into the cooling jacket that connects the cooling system with the grinding jar for continuous cooling before and during shredding. The grinding jar performs radial oscillations in a horizontal position making the grinding ball to impact with high energy on the sample material at the rounded ends of the grinding jar and therefore pulverize it (Retsch, 2020a).

Cryomill provides programmable shredding conditions depending on the configuration settings and the feed material, which enables to adjust the cost of the process (Retsch, 2011). There is a number of grinding parameters that can be set to create several cryomill programs: i) vibration frequency in a range of 5-30 Hz; ii) grinding duration in a range of 0.5-99 min; iii) intermediate cooling duration in a range of 0.5-99 min (usually the grinding and cooling duration is set at similar levels); and iv) number of cooling/grinding cycles which can be ranged from 1 to 9. The control unit of cryomill has memory or 9 shredding programs (Retsch, 2020a).

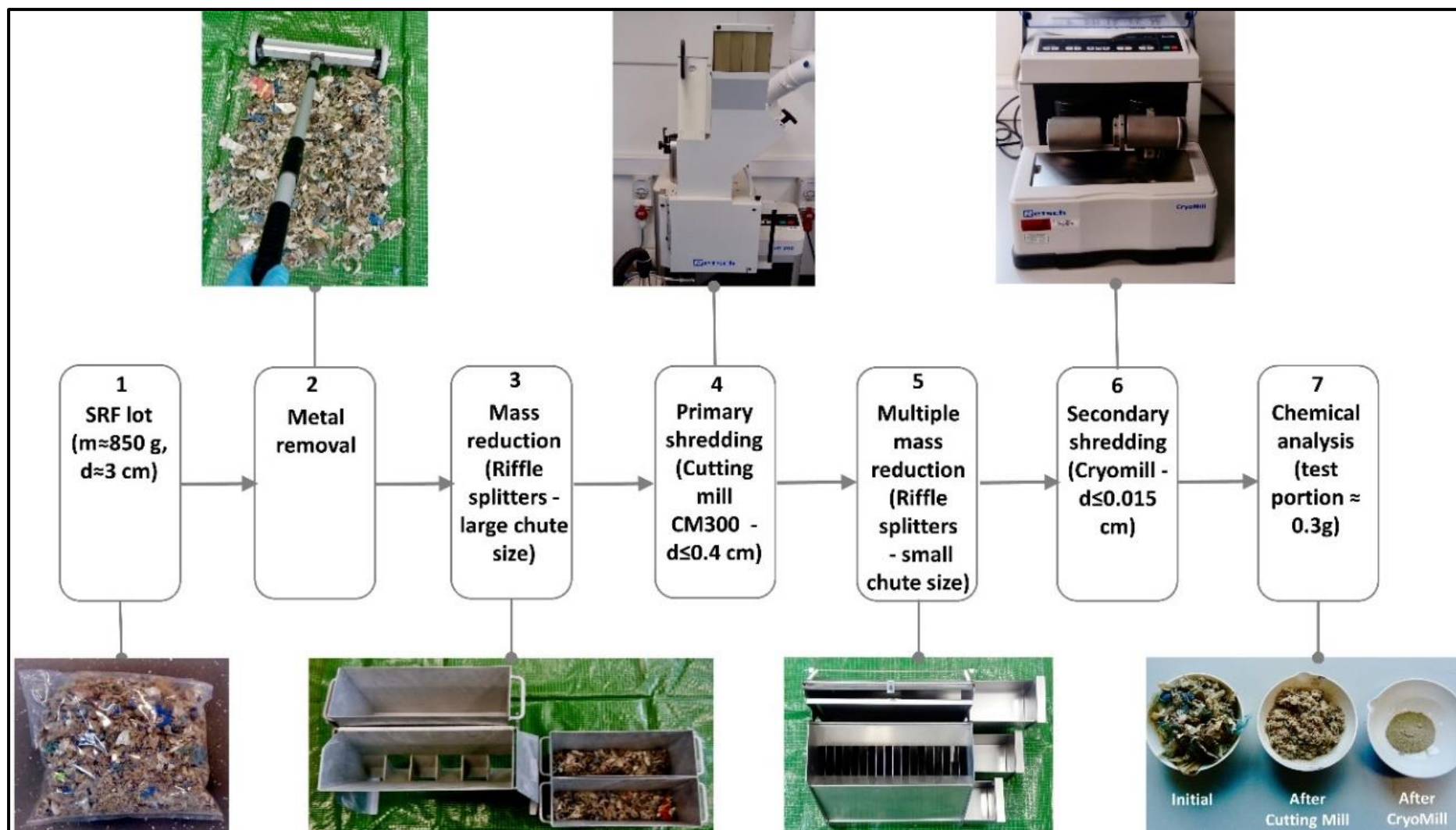


Figure 4-4. Sub-sampling protocol applied to SRF for quality characterization: operations and equipment were informed by best practices according to the ToS (riffle splitting, advanced shredding processes and skilled operator).

4.2.3 Quantification of ToS-formula factors

The factors required for the calculation of the sampling constant, C (**Eq. 2-4**) after each stage of shredding were determined as follows:

Liberation factor (l): For the heterogeneous SRF, the value 1 was selected, as the maximum value is recommended for environmental applications (Gerlach and Nocerino, 2003). After primary shredding the value was set at 0.8 (considered as *very heterogeneous material*) and after secondary shredding at 0.4 (considered as *heterogeneous material*). The selection of these values was based on the optical observation of color uniformity in SRF sub-samples after each shredding process and the guidance on the liberation parameter estimates provided by ToS (see **Appendix A**).

Shape factor (f): SRF mainly manufactured from MSW is a fluff-type material and a value of 0.05 is recommended by BS EN 15442 (2011). It was selected the 0.2 (*soft homogeneous such as gold flakes*) and 0.5 (*all particles are spheres such as minerals*) for the stages of primary and secondary shredding, respectively. These values were selected based on the optical observation of the particle's shape of sub-samples and on characteristic values of shape parameters for several materials given by ToS (see **Appendix A**).

Granulometric factor (g): According to BS EN 15442 (2011), the g factor should be kept at 0.25 for PSD $d_{95}/d_{05} > 4$. Even after secondary shredding this ratio was higher than four (results presented in **Section 5.4.1.1**), so the factor remained constant.

Mineralogical factor (c): **Eq. 2-5** needs to define Total [Cl] of the sample and the density both of SRF and particles containing the Cl. The arithmetic mean of Total [Cl] in 16 sub-samples constituted the concentration of critical component (a_L). The most prevalent chlorinated compounds in MSW were considered for the calculation of the density of particles containing Cl in SRF (λ_M): PVC and NaCl with density 1.38 and 2.17 g cm⁻³, respectively (Ma et al., 2010; PubChem, 2019; Guo et al., 2001). Literature findings from the first part of critical review (**Section 4.1.1**) showed that 50-75% w/w of Total [Cl] in MSW mainly attributed to the presence of plastics and 25-50% w/w mainly attributed to the presence of food waste (**Table 5-1**). Assuming that 75% of Total [Cl] was due to PVC and 25% was due to NaCl, as the fraction of plastics in SRF can be higher than in MSW due to

sorting processes applied in MT/MBT plant. The weighted average of PVC and NaCl set the λ_M value at 1.58 g cm^{-3} . The SRF density was set at 0.15 g cm^{-3} (DD CEN/TS 15401, 2010).

Noted that the above selected values of sampling factors were used only as estimators based on ToS and SRF characteristics. The precise quantification of these factors is difficult as a significant amount of information, not available here, is required for the target material (Ramsey and Thompson, 2007). The purpose of theoretical ToS calculations was the quantification of the effects of alternative shredding scenarios and not the precise calculation of FE.

4.2.4 ToS-based uncertainty for different sample preparation scenarios

The FE was calculated based on three hypothetical sample preparation scenarios: *sub-sampling without shredding (NS)*, where only riffle splitting would take place; *sub-sampling with only primary shredding (PS)*, where riffle splitting and only primary shredding (with cutting mill) after the first stage of riffle splitting would take place; and *current sub-sampling plan (CS)*, where riffle splitting and both primary and secondary shredding, took place following the sub-sampling protocol (**Section 4.2.2**). Specifically, nomographs were constructed that depicted the trend of s_{FE}^2 as a function of sample mass during sub-sampling for the three different shredding scenarios. Nomographs can be designed by recasting the ToS-formula (**Eq. 2-3**): for a given particle size, plotting the logarithm of the variance of FE versus the logarithm of the sample mass results in a straight line with a slope of minus one (Gerlach and Nocerino, 2003). The comparison amongst the different shredding scenarios led to quantitatively determine the impact of shredding on the sub-sampling uncertainty based on ToS formula (**Eq. 2-3**).

Special attention was paid to cryomill due to its effective shredding ability and confined laboratory application. The effect of several configuration settings provided by the cryomill on the FE was examined, so that to select the most suitable shredding program. Specifically, four cryomill programs were selected including a range of shredding procedures from brief to more extensive programs: i) program with 2 grinding cycles, 2 min grinding time, 1 min intermediate cooling and 30 Hz grinding frequency (P2); ii) program with 4 grinding cycles, 2 min grinding time, 1 min intermediate cooling

and 30 Hz grinding frequency (P4); iii) program with 5 grinding cycles, 2 min grinding time, 2 min intermediate cooling and 30 Hz grinding frequency (P5); and iv) program with 9 grinding cycles, 2 min grinding time, 2.5 min intermediate cooling and 25Hz grinding frequency (P9). Common metrics of PSD, such as d_{90} , d_{50} , d_{10} and span, were used to statistically compare the shredding programs. The span expresses the width of distribution and gives an indication of how far the diameter of 10% (d_{10}) and 90% (d_{90}) of particles are apart, normalized with the midpoint (d_{50}) (Horiba, 2012). The FE emerging from: the final stage of sub-sampling (from test sub-sample (7 g) to test portion (0.3 g)); and the entire sub-sampling (from the initial sample (850 g) to test portion (overall FE)) was calculated. The d_{90} of each cryomill program was used to calculate the FE based on ToS formula (**Eq. 2-3**).

4.2.5 Incorrect sub-sampling practices

Despite the calculation of FE that provides the minimum uncertainty under a perfect sub-sampling process, practices that may introduce bias and increase the uncertainty arising from sub-sampling were monitored. Specifically, three main aspects of incorrect sub-sampling practices mostly related to shredding were checked: i) loss of sample mass by weighing individually the sub-samples after each step of sub-sampling; ii) evaporation of moisture during primary and secondary shredding by obtaining 3 test sub-samples of 7 g with riffle splitters from a pre-dried sub-sample of 50 g and taking 6 replicates of residual moisture thereupon pre-drying, before and after each shredding process; and iii) analytical error respecting Cl recovery by using reference materials. Synthetic mixtures with known composition and consequently Total [Cl] resembling the composition of SRF were prepared and analysed. Specifically, two mixtures composed of powered biomass polymers, such as cellulose, xylan (common type of hemicellulose) and lignin, and plastic polymers, such as HDPE, PP, PET and PVC with Total [Cl] 0.62% w/w and 1.42% w/w, respectively, were prepared. The presence of Cl in the synthetic mixtures was attributed only to the presence of PVC with Total [Cl] 53.7% w/w.

The recovery of Cl (R) is given by the following equation (Prichard and Barwick, 2007):

$$R(\%) = \frac{\bar{x}}{x_0} * 100 \quad \text{Eq. 4-1}$$

where R (%) is the Cl recovery, $\bar{x}$ is the mean value of Total [Cl] obtained from analysis and x_0 is the assigned Total [Cl].

The analytical results of Total [Cl] in SRF sub-samples were corrected as shown below:

$$C_{cor} = \frac{C_{obs}}{R(\%)} * 100 \quad \text{Eq. 4-2}$$

Where C_{cor} is the corrected measurement result, C_{obs} is the observed measurement result and $R(\%)$ is the recovery of Cl.

4.2.6 Balanced-nested design for sub-sampling simulation

The balanced nested design simulated the stages of the established sub-sampling process for the obtainment of one test sub-sample, which is the case in sub-sampling. Each stage of sub-sampling indicates the operation of riffle splitting, which creates nested sub-samples within the sample. For example, in the 1st stage of sub-sampling, the sample was split into sub-samples A and B (nested within the sample), in the 2nd stage sub-samples A and B were shredded and split into sub-samples A1 and A2 (nested within A) and B1 and B2 (nested within B), respectively, etc. Sub-samples are nested because they depend only on the sample (or higher level sub-sample) from which they came from (Krzywinski et al., 2014).

Specifically, two balanced nested designs were developed: *Gross_nested* to simulate the sub-sampling process from the 1st stage to the 4th stage of sub-sampling (four-level balanced nested design); and *Intra_nested* to simulate the sub-sampling process from the 5st stage to the 7th stage of sub-sampling (three-level balanced nested design) (**Figure 4-5**). In *Gross_nested* design, the SRF sample with a mass 850 g was split 4 times to obtain 16 sub-samples of 53 g. Thereafter a test sub-sample of 6-7 g was taken from each sub-sample of 53 g with riffle splitters and 3 replicates were taken for analysis. *Gross_nested* design examined the ability of a sub-sample of 53 g to represent the initial SRF sample of 850 g (sub-sampling uncertainty from 1st to 4th stage). *Gross_nested* design was applied in the first part of methodology to assess the impact of shredding and establish a sub-sampling plan (**Section 4.2.2**). Similarly, in *Intra_nested* design, a SRF sub-sample with a mass 53 g was split 3 times to

obtain 8 test sub-samples of 6-7 g. *Intra_nested* design examined the ability of the test sub-sample of 6-7 g to represent the SRF sub-sample of 53 g (sub-sampling uncertainty from 5th to 7th stage).

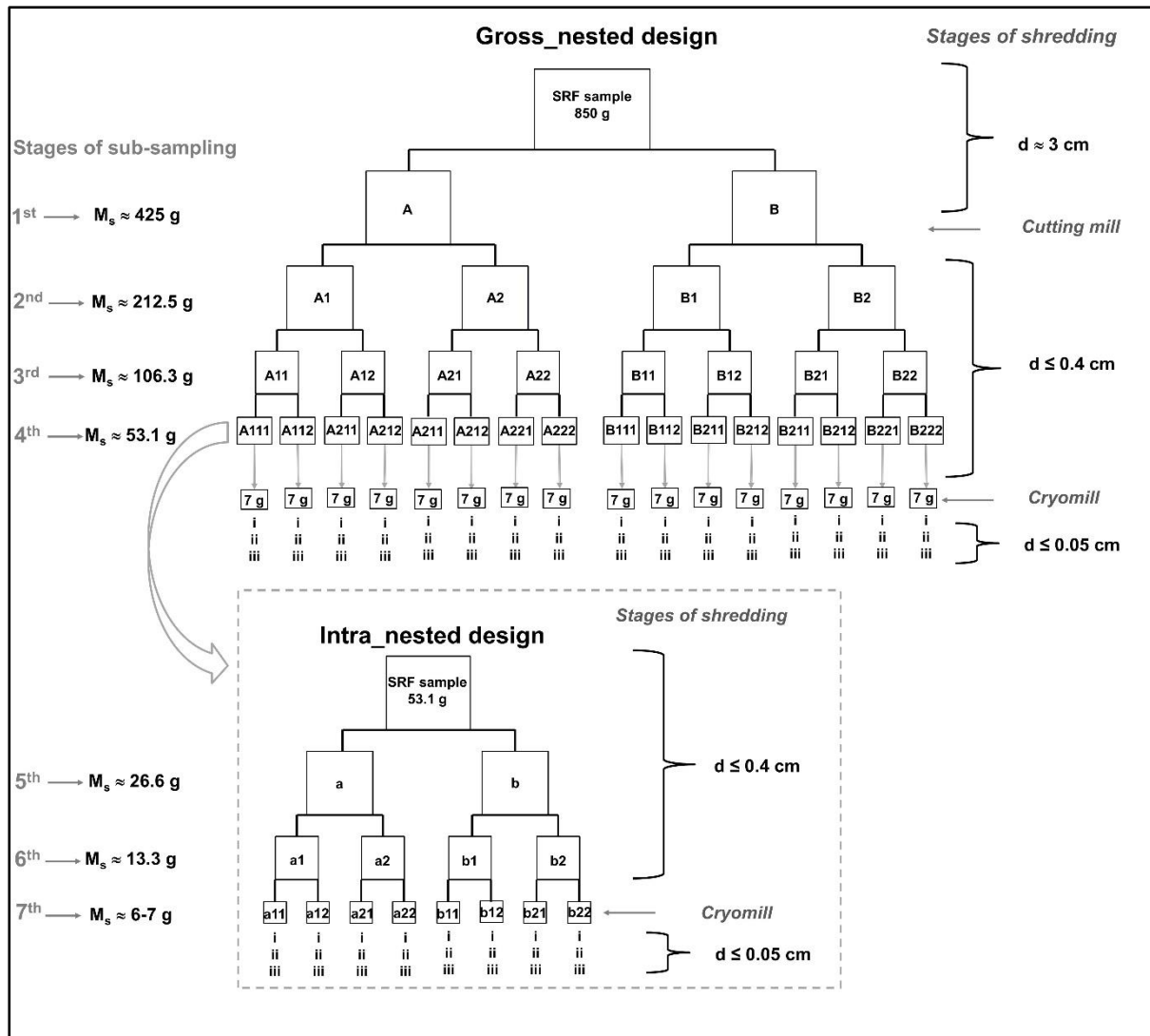


Figure 4-5. Four-level balanced nested design for the calculation of the uncertainty arising from the 1st to the 4th sub-sampling stage (*Gross_nested*: from the sample mass of nearly 850 g to the sub-sample of 53 g) and three-level balanced nested design for the calculation of the uncertainty arising from the 5th to the 7th sub-sampling stage (*Intra_nested*: from the sub-sample of 53 g to the sub-sample of 6-7 g). In every sub-sampling stage, sub-samples depend only on the lower level of nested sub-samples. *Gross_nested* and *Intra_nested* design consists of 16 and 8 test sub-samples, respectively. Three replicates for each test sub-sample were taken to capture the uncertainty arising from analysis (AE).

Despite the 7 stages of sub-sampling which include all riffle splitting and shredding operations – reported as SE following the terms of ToS (**Eq. 2-2**), the sub-sampling plan included also a stage of sub-sampling for the obtainment of replicate measurements. This stage contains an uncertainty due to both mass reduction from test sub-sample to test portion and AE as specified by ToS. Herein, this

stage is referred to AE. Based on ToS, AE is only due to analysis, but the sub-sampling for the obtainment of replicates could not be separated by AE (**Section 2.5.1.3**). Noted that the AE provides the level of precision of analytical measurements. The combination of these two nested designs is illustrated in **Figure 4-5**.

The names of samples at each level of both nested designs is presented in **Table 4-2** and sample characteristics at each stage of sub-sampling along with the used equipment is presented in **Table 4-3**.

Table 4-2. Sub-samples naming at each stage of sub-sampling (mass reduction processes) along with the level of nested layout in both designs: *Gross_nested* and *Intra_nested*.

Nested design	Stage of sub-sampling	Grouping level of sub-samples	Name of samples
<i>Gross</i>	1 st	groups	A, B
	2 nd	sub-groups	A1, A2, B1, B2
	3 rd	sub-sub-groups	A11, A12, A21, A22, B11, B12, B21, B22
	4 th	sub-sub-sub-groups/ test sub-samples	A111, A112, A121, A122, A211, A212, A221, A222, B111, B112, B121, B122, B211, B212, B221, B222
	Analysis*	Test portions	A111i, A111ii, A111iii, A112i...
<i>Intra</i>	5 th	groups	a, b
	6 th	sub-groups	a1, a2, b1, b2
	7 th	sub-sub-groups/ test sub-samples	a11, a12, a21, a22, b11, b12, b21, b22
	Analysis*	Test portions	a11i, a11ii, a11iii, a12i...

*The stage of analysis includes the obtainment of three test portions from the test sub-sample of 6-7 g

Table 4-3. Sample characteristics including sample mass (M_s) and sample size (d_{90}) at each stage of the established sub-sampling plan for SRF quality characterisation induced by consecutive sub-sampling operations along with the related equipment.

Sample	Operation	Equipment	Operation stage	Initial M_s (g)	Final M_s (g)	d_{90} (cm)
Initial sample	Pre-drying	Drying cabinet	Single	1,000	850	3
1 st sub-sample	Mass reduction	Riffle divider	1 st	850	425	3
1 st sub-sample	Shredding	Cutting mill	Primary	425	425	0.4
2 nd sub-sample	Mass reduction	Riffle divider	2 nd	425	212.5	0.4

Sample	Operation	Equipment	Operation stage	Initial M _s (g)	Final M _s (g)	d ₉₀ (cm)
3 rd sub-sample	Mass reduction	Riffle divider	3 rd	212.5	106.2	0.4
4 th sub-sample	Mass reduction	Riffle divider	4 th	106.2	53.1	0.4
5 th sub-sample	Mass reduction	Riffle divider	5 th	53.1	26.5	0.4
6 th sub-sample	Mass reduction	Riffle divider	6 th	26.4	13.2	0.4
7 th sub-sample	Mass reduction	Riffle divider	7 th	13.2	6.6	0.4
Test sub-sample	Shredding	Cryomill	Secondary	6.6	6.6	0.015
Test portion	Analysis	See Section 4.2.7.2	Single	6.6	0.01 – 1*	0.015

* Test portion is different for each SRF property; more information is given in **Section 4.2.7.2**

I broke the nested design into two complementary designs due to the small capacity of cryomill (50 ml), which cannot fill more than 6-7 g of SRF. It would be considerably expensive and time-consuming to accurately divide 850 g into all possible test sub-samples of 6-7 g. This would correspond to more than 130 test sub-samples. The decision to break the nested design at the 4th stage was taken after checking the minimum number of test sub-samples following riffle splitting (**Table 4-4**).

Table 4-4. Number of sub-samples required for both nested designs based on 7 possible scenarios of SRF sub-sampling depending on the sub-sample mass of the final stage of sub-sampling in *Gross_nested* design and sample mass of the first stage in *Intra_nested* design applying riffle splitting for mass reduction processes – sub-sampling: scenario 4th was selected.

Scenario	Initial SRF sample mass	Final sub-sample mass ¹	No. test sub-samples			No. total measurements*
			Gross ²	Intra ³	Total	
1 st		425	2	66	68	204
2 nd		213	4	32	36	108
3 rd		106	8	16	24	72
4th	From 850 g to:	53	16	8	24	72
5 th		27	32	4	38	114
6 th		13	64	2	66	198
7 th		6.5	131	-	131	393

¹Indicates the sub-sample mass at the final stage of sub-sampling in *Gross_nested* and at the first stage of sub-sampling in *Intra_nested* after riffle splitting; ²At each scenario, test-subsamples derived by dividing the initial sample mass (850g) by the final sub-sample mass of *Gross_nested* (e.g. by 53 g in the 4th scenario, etc.); ³Similarly, test-subsamples derived by dividing the final sub-sample mass from *Gross_nested* (e.g. 53g) by the final sub-sample mass of 6-7g; *Three replicates for each test sub-sample

4.2.7 Process variables – analytical techniques of DoE1

In this section, the critical parameters selected for the empirical and theoretical quantification of sub-sampling uncertainty along with the analytical techniques for their determination are described. Based on ToS, the sampling uncertainty depends on the fraction of particles that contain the analyte resulting from the concentration and the density of particles that contain the analyte (**Eq. 2-5**). When the fraction of particles that contain the analyte is relatively low, the distribution of the analytical results tends to look more like a Poisson distribution rather than a Gaussian indicating the need for extended sampling process (Gerlach and Nocerino, 2003). The selected SRF properties were analysed following the British standards stipulations for SRF characterization.

4.2.7.1 Critical SRF properties

Typical properties of SRF related to economic and technical attributes were selected for the quality determination of SRF including: moisture content (MC) – an economic attribute; ash content (Ash) – a technical attribute; NCV – an economic attribute; Total [Cl] – a technical attribute; and SRF combustion behaviour using TG-DTG.

In relation to the latter, the combustion behaviour of SRF was statistically processed using both: i) the entire TG-DTG signal consisting of 10,442 points – measurements of both mass (TGA: 5,221) and rate of mass change (DTG: 5,221) at each second); and ii) critical measurement variables able to capture the greatest part of information.

In relation to ii), I selected points that could be eventually used to draw an approximate smoothed TG-DTG curve that captures important patterns in the dataset. Along with recommendations of laboratory technicians, expert in thermal analysis, 37 thermal critical points were selected able to characterise the combustion behaviour of the sample. These critical TG-DTG points are described in **Table 4-5**. The first 21 points (1-21) were obtained by TG signal, whereas the remaining 16 points (22-37) were taken by DTG signal. An additional measurement variable was also included that is widely applied in studies that conducted TGA under oxidative conditions (Tabarés et al., 2000; Lin et al., 2015; Wang et al., 2012; Wang et al., 2009) – referred to as combustibility index (S). This index is considered as a

unique value for each TG-DTG curve and therefore it can be used to evaluate the combustion behaviour of the sample (Lin et al., 2015). It is defined as:

$$S = \frac{(\frac{dw}{dt})_{max}(\frac{dw}{dt})_{mean}}{T_i^2 T_f} \quad \text{Eq. 4-3}$$

where $(\frac{dw}{dt})_{max}$ and $(\frac{dw}{dt})_{mean}$ are the maximum and mean rate of weight loss, respectively, expressed in % w/w min⁻¹, while T_i and T_f are the inflection temperature of the first DTG peak and endset temperature of the final DTG peak, respectively. Combustibility index is a comprehensive combustion parameter expressed in % w/w min⁻² °C⁻³.

Table 4-5. Combustion characteristic points obtained from the TG-DTG curve that were used for the statistical quantification of sub-sampling uncertainty for TG-DTG of SRF.

No.	Critical points of TG-DTG curve	Description
1	T _{10%}	Temperature in which the weight loss of the sample is 10% w/w (°C)
2	T _{20%}	Temperature in which the weight loss of the sample is 20% w/w (°C)
3	T _{30%}	Temperature in which the weight loss of the sample is 30% w/w (°C)
4	T _{50%}	Temperature in which the weight loss of the sample is 50% w/w (°C)
5	T _{75%}	Temperature in which the weight loss of the sample is 75% w/w (°C)
6	Res.MC	Residual moisture content of the sample (% w/w) after pre-drying
7	Res.MC_Inf.T	Inflection temperature of the moisture DTG peak (°C)
8	Res.MC_Mid.T	Midpoint temperature corresponding to 50% w/w of weight loss induced at moisture DTG peak (°C)
9	1st_ML	Mass loss induced in 1st DTG peak (% w/w)
10	1st_Inf.T*	Inflection temperature of the 1st peak (°C)
11	1st_Mid.T	Midpoint temperature corresponding to 50% w/w of weight loss induced at 1st DTG peak (°C)
12	2nd_ML	Mass loss induced in 2nd DTG peak (% w/w)
13	2nd_Inf.T*	Inflection temperature of the 2nd DTG peak (°C)
14	2nd_Mid.T	Midpoint temperature corresponding to 50% w/w of weight loss induced at 2nd DTG peak (°C)
15	3rd_ML	Mass loss induced in 3rd DTG peak (% w/w)
16	3rd_Inf.T*	Inflection temperature of the 3rd DTG peak (°C)
17	3rd_Mid.T	Midpoint temperature corresponding to 50% w/w of weight loss induced at 3rd DTG peak (°C)
18	4th_ML	Mass loss induced in 4th DTG peak (% w/w)
19	4th_Inf.T*	Inflection temperature of the 4th DTG peak (°C)
20	4th_Mid.T	Midpoint temperature corresponding to 50% w/w of weight loss induced at 4th DTG peak (°C)

No.	Critical points of TG-DTG curve	Description
21	Res.	Residue (% w/w)
22	1st_RML	Maximum rate of mass loss at 1st DTG peak (% w/w min ⁻¹)
23	1st_On.T	Onset temperature of the 1st DTG peak (°C)
24	1st_Peak.T	Peak temperature of the 1st DTG peak (°C)
25	1st_End.T	Endset temperature of the 1st DTG peak (°C)
26	2nd_RML	Maximum rate of mass loss at 2nd DTG peak (% w/w min ⁻¹)
27	2nd_On.T	Onset temperature of the 2nd DTG peak (°C)
28	2nd_Peak.T	Peak temperature of the 2nd DTG peak (°C)
29	2nd_End.T	Endset temperature of the 2nd DTG peak (°C)
30	3rd_RML	Maximum rate of weight loss at 3rd DTG peak (% w/w min ⁻¹)
31	3rd_On.T	Onset temperature of the 3rd DTG peak (°C)
32	3rd_Peak.T	Peak temperature of the 3rd DTG peak (°C)
33	3rd_End.T	Endset temperature of the 3rd DTG peak (°C)
34	4th_RML	Maximum rate of mass loss at 4th DTG peak (% w/w min ⁻¹)
35	4th_On.T	Onset temperature of the 4th DTG peak (°C)
36	4th_Peak.T	Peak temperature of the 4th DTG peak (°C)
37	4th_End.T	Endset temperature of the 4th DTG peak (°C)

* The inflection temperature from TG signal corresponds to the peak temperature of DTG signal (Kalsoom, 2014).

4.2.7.2 Analytical techniques of DoE1

A set of established analytical techniques – most of them standardized – were applied to determine properties of SRF and therefore address the objectives of DoE1 methodological part:

I. Particle size distribution (PSD): Wet laser diffraction analysis was used to determine the PSD of the test sub-samples shredded by cryomill under different configuration settings (**Section 4.2.4**) following the selected sub-sampling protocol (**Section 4.2.2**). Measurements performed by Mastersizer (Mastersizer 2000E EPA2000, Malvern, UK) with a wet dispersion unit (hydro 2000SM, Malvern, UK) with a particle sizing range of 0.01-10000 µm. A small amount of test sub-sample (0.5-1 g) was diluted with 120ml of propan-2-ol (isopropyl-alcohol) used as liquid dispersant in a beaker and added to the dispersion unit tank. The dispersion unit delivered the dispersed sample to the optical bench that captures the scattering pattern from the particles passing through a laser beam taking ca. 2000 snaps for each measurement (5 seconds). During laser diffraction the sample was circulated between the dispersion unit and the optical bench through the

cell. The raw data from the optical bench analysed by the Mastersizer 2000 software connected with the system that provided the percentage of volume of sample above a certain particle size (Malvern, 2021). The average of five replicate measurements was taken for each cryomill program (**Section 4.2.4**).

II. Moisture content (MC): The determination of MC in commercially produced SRF samples is a straightforward and well-established technique performed in drying ovens, where the loss of mass is reported as MC (BS EN 15414-3, 2011). The sample was pre-dried in a large scale drying oven (Genlab™ DC 1000) before sample preparation and sub-sampling (**Section 4.2.2**) for bulk pre-drying. The samples were weighted before and after pre-drying in a balance (METTLER TOLEDO) with 0.1 g readability to determine the bulk MC. Following the sub-sampling protocol (**Section 4.2.2**) up to step 5 before secondary shredding (**Figure 4-4**), the residual MC was determined by placing test portions (1 g) in weighing dishes in a drying oven (Carbolite, PN120) at 105 °C until constant mass was reached – herein for 24h. Test portions were weighted before and after drying in a balance (METTLER TOLEDO) with 0.1 mg readability to determine the residual MC. The average of three replicate measurements was taken for each test sub-sample. The total MC, expressed in % w/w, was calculated as follows:

$$MC_{Total} = MC_b + MC_{residual} \left(1 - \frac{MC_b}{100}\right) \quad \text{Eq. 4-4}$$

Where, MC_b is the bulk moisture – the moisture that was evaporated during pre-drying, and $MC_{residual}$ is the remaining moisture after pre-drying. The content of moisture was calculated manually by dividing the mass loss after drying by the initial weight.

III. Net calorific value (NCV): The NCV in SRF, expressed in MJ kg^{-1} on a dry basis (MJ kg^{-1}_d), measured with the standardised analytical technique BC (BS EN 15400, 2011) in a bomb calorimeter system (6200 Isoperibol calorimeter, Parr, USA) with a standard oxygen bomb (1108 oxygen bomb, Parr). Following the sub-sampling protocol (**Section 4.2.2**), test portions (0.3 g) were obtained using a semi microbalance (METTLER TOLEDO) with 0.01 mg readability. These amounts were pelletised to ensure homogeneity before analysis by a pellet press device (FRITSCH, Germany) under 2.5 tonnes of pressure. Pellets poured with one drop of kerosene

(spike) to promote complete combustion and their weights were recorded before and after spiking. Each pellet was placed in a crucible loaded onto the hangdown of the bomb, while a fuse wire of 10 cm was inserted between the two electrodes of the bomb to ignite the sample. The walls of the bomb were rinsed with 10 ml of KOH solution with molarity 0.2 mol l^{-1} to absorb halogenated compounds. The lid of the bomb was screwed on and the valve was closed. After that, the bomb was filled with oxygen through the gas fill line so that combustion takes place in a high-pressure oxygen environment (3 MPa). The next step was to place the bomb in the bucket filled with 2 L of water inside the calorimeter. Two ignition wires were attached to the head of the bomb and the lid of calorimeter was closed. In the control menu of the system displayed to a small screen onto the calorimeter, the weights of pellet and spike were inserted and the ignition was started. When the temperature was stabilised, NCV was automatically displayed on the screen based on the rise temperature after ignition (BS EN 15400, 2011). After the completion of the experiment, the bomb was removed from the bucket and the gas was released over one minute in the fume hood. The average of three replicate measurements was taken for each test sub-sample.

IV. Total chlorine concentration (Total [Cl]): The Total [Cl] in SRF, expressed in % w/w on a dry basis (% w/w_d), measured by combining the standard method BC (BS EN 15400, 2011) with the photometric method of Palintest Chloridol test (Palintest-Test instructions, 2019). After BC, the residues into the bomb (10 ml KOH and any solid residue) were collected into labelled falcon tubes by rinsing the bomb and crucible three times with UHQ H₂O. Specifically, the residues diluted to 50 ml (1:5 dilution ratio). These solutions were filtered by syringe filters with a 0.22 µm pore size. From the filtered solutions, 1ml poured in test tubes and diluted to 10ml of UHQ H₂O (1:10 dilution ratio) leading to an overall dilution ratio 1:50 of the initial absorbing solution introduced into the bomb (10 ml KOH) – a recommended ratio for the determination of Total [Cl] in SRF (BS EN 15408, 2011). After this step of sample preparation, Palintest Chloridol test was carried out based on a tablet reagent system containing silver nitrate (Palintest-Test instructions, 2019). Tablets of silver nitrate were added into the test tubes along with the diluted solutions. Silver nitrate reacted with the chlorides absorbed by KOH producing silver chloride. The insoluble silver chloride observed as turbidity in test solutions was measured by the photometer (Palintest

photometer 7100) with a Cl detection range of 0-50 mg l⁻¹. The degree of turbidity was proportional to the chloride concentration provided by photometer. These concentrations were multiplied by 50 (dilution ratio 1:50) to obtain the Total [Cl] in SRF. The average of three replicate measurements was taken for each test sub-sample. **Ash content ('Ash'):** The determination of 'Ash' in SRF, expressed in % w/w on a dry basis (% w/w_d), was determined using a muffle furnace (Carbolite, CFW 12/23). Following the sub-sampling protocol (**Section 4.2.2**) up to step 5 before secondary shredding (**Figure 4-4**), test portions (1g) were placed in porcelain dishes with a depth 20 mm. Weights of test portions and dishes were recorded using a balance (METTLER TOLEDO) with 0.1 mg readability. Test portions were heated in air atmosphere under a specific heating routine: i) raise of furnace temperature under a heating rate of 5 °C/min up to 250 °C and maintain this temperature for 60 min; and ii) temperature raise up to 550 °C and maintain this temperature for 120 min (BS EN 15403, 2011). After incineration, the weights of residues were recorded and 'Ash' in SRF was determined according to BS EN 15403 (2011) by dividing the mass loss after incineration by the initial dry weight. The average of three replicate measurements was taken for each test sub-sample.

- V. Thermogravimetric analysis combined with the derivative of TGA signal (TG-DTG):** TG-DTG experiments were performed by using a TGA apparatus (METTLER TOLEDO TGA/ DSC 3+) that measures the mass loss of the sample (% w/w) as a function of temperature under non-isothermal operating conditions: atmosphere of thermal decomposition: air; flow rate: 50 ml min⁻¹; heating rate: 10 °C min⁻¹; sample holder: alumina 150 µl crucibles; maximum temperature: 900 °C; test portion mass: 10 mg. These conditions were selected respecting the literature findings from the second part of critical review (**Section 4.1.2.2**). The reason that oxidative conditions were used instead of inert atmosphere was to quantify the uncertainty for the determination of SRF thermal behaviour in co-combustion applications. Following the sub-sampling protocol (**Section 4.2.2**), test portions were obtained using a semi microbalance (METTLER TOLEDO) with 0.01 mg readability. The crucibles contained test portions were placed in auto-sampler robot able to process up to 17 samples providing unattended measurements. The duration of each experiment (analysis of each test portion) was ca. 3 hours. Three replicate measurements were taken for each test sub-

sample. The steps of analysis including definition of operating conditions, insertion of test portions (position number in auto-sampler, sample weight and crucible weight), data handling and obtainment of analytical results were accomplished using the STAR^e software. Considering the needs of DoE1 (**Table 4-5**), an evaluation recorder (referred to EvalMacro) was created using a variety of evaluation possibilities such as the first derivative (DTG-curve) and graphic evaluations (critical points of TG-DTG curves) offered by the software (METTLER TOLEDO, 2021).

4.2.8 Statistical analysis – Software

To give a coherent description of statistical analysis, it was splitted it into three main parts which are presented in the following sub-sections explaining the statistical tools used to meet the related research objectives.

4.2.8.1 Statistical analysis to establish a sub-sampling plan

At this stage, one-way ANOVA was conducted to statistically compare: the 4 different cryomill programs with respect to PSD metrics; and the moisture content of sub-samples before and after each shredding process (TIBCO StatisticaTM 13.3.0 software). The key requirements to use ANOVA were checked: normal distribution of residuals and raw data with the Anderson-Darling test (Harwell et al., 1992); homogeneity of variance with Levene's test (Glass and Hopkins, 1996); and independence of errors by implementing randomization during sub-sampling and chemical analysis (Montgomery, 2017). Randomization to reduce bias was applied by analysing sub-samples by chance rather than by choice (Prichard and Barwick, 2007). Specifically, test samples were analysed by generating a random permutation of a sequence independently the order of sample's labelling (e.g. A111, A112, A121, A122, A211, A212, etc.). A brief knowledge background on the key requirements to use ANOVA is provided in **Appendix B**.

Graphical illustrations were designed to assess the experimental results derived from the analysis of 16 test sub-samples, in which three test portions obtained for the determination of Total [Cl] and MC in SRF sample. Specifically, 95% confidence interval error bars of mean values for each test sub-sample were designed to assess the precision of analytical measurements. Additionally, boxplots were

designed to provide the dispersion of Total [Cl] and MC arising from the average values of test sub-samples and classify the initially obtained SRF sample based on the classification scheme (BS EN 15359, 2011).

The possibility to obtain a representative test sub-sample following the established sub-sampling plan for determination of Total [Cl] was determined by calculating the confidence interval for binomial proportions with three different methods (normal approximation, exact Clopper-Pearson and Wilson score method). The results were based on the Wilson score method as it provided robust and effective means for estimating intervals (Wallis, 2013). Further details can be found in **Appendix C1**.

The possibility to obtain representative test sub-samples for determination of Total [Cl] in SRF implementing the established sub-sampling protocol was determined following two assumptions: i) the acceptable limit of uncertainty in order to say that a test sub-sample is representative was 15%; and ii) the average Total [Cl] derived from 16 test sub-samples represented the real Total [Cl] in the sample – the true value.

In relation to the first assumption, an overall $FE \leq 15\%$ is a recommended acceptable reference limit (Gerlach and Nocerino, 2003; Dominy et al., 2018b; Dominy et al., 2019), although the limit value depends on the fitness for purpose requirements that are different for each application (Ramsey and Thompson, 2007). Dominy et al. (2019) discussed the sampling methods used in underground grade control through the application of ToS providing a number of examples. It was provided a risk review for a low coarse gold mineralisation grade control sampling programme indicating that a sampling uncertainty $>15\%$ was high, between 5 and 15% was moderate and $<5\%$ was low/acceptable (Dominy et al., 2019). In relation to the second assumption, the average value of Total [Cl], which was actually the average from *Gross_nested* design with the 16 test sub-samples and three replicates each, constituted an estimate of the true value. The mean value contains always an uncertainty unless the entire sample mass is analysed. However, calculation of the mean value which is the most common approach can lead to a representative estimation of the true value by using a set of means (Slowinski et al., 2015), such as here with 16 means derived from the 16 sub-samples.

4.2.8.2 Statistical analysis to quantify the sub-sampling uncertainty for MC, Ash, Total [Cl] and NCV in SRF

It was statistically quantified the overall uncertainty emerging from sample constitutional heterogeneity, sub-sampling process and analysis and the uncertainty arising from each sub-sampling stage. Nested ANOVA at a significance level 0.05 was conducted in TIBCO Statistica™ 13.3.0 software for both designs: four-level nested ANOVA for *Gross_nested* and three-level nested ANOVA for *Intra_nested* design (analytical results of critical SRF properties that formed datasets for nested-ANOVA is presented in **Appendix D2**) The knowledge background on nested – ANOVA is presented in **Appendix D1**. Each level of nested-ANOVA referred to each stage of sub-sampling and compared the mean values between sub-samples nested within the sample or higher level of sub-sample. Significance results of nested-ANOVA detected the statistical difference at each stage and post hoc tests were carried out (**Appendix D1**) to detect the sources of the difference (pairs in which nested sub-samples are significantly different to each other) (Tian et al., 2018). Key assumptions required to use ANOVA were examined (**Appendix D3**).

In every stage of sub-sampling, the mean values of sub-samples derived from the mean values of the lower level of nested sub-samples capturing the variance introduced at each level, known as variance components. The relative standard deviation (RSD) of these variances provided evidence for the uncertainty arising from each stage of sub-sampling process. The RSD of the sum of the variance components corresponded to the overall uncertainty. The variance components given by nested ANOVA exhibited the contribution of each sub-sampling stage to the overall uncertainty, which was calculated by dividing the variance from each stage (component variance) by the overall variance (summation of variance components) (Montgomery, 2017). This information gave insights on which stages affected mostly the overall sub-sampling uncertainty.

In addition, descriptive statistics were used to summarize the analytical results, excluding TG-DTG, of the SRF properties obtained through the established sub-sampling process (arithmetic mean, median, standard deviation, 95% confidence interval and range). Descriptive statistics derived from the average values of 17 sub-samples: 16 sub-samples analyzed in *Gross_nested* design and 1 sub-sample analyzed in *Intra_nested*. At this stage, I also included the NCV on wet basis so that to

characterize the SRF sample according to the classification system (BS EN 15359, 2011). However, the sub-sampling uncertainty was not quantified for the properties on a wet basis as it would include the uncertainty for moisture, which was obtained separately.

Along with the statistical quantification of uncertainty at each stage of sub-sampling, ToS formula (**Eq. 2-3**) was used to theoretically calculate the minimum sub-sampling uncertainty for the selected SRF properties based on ToS. This comparison would give insights into the suitability of ToS in sub-sampling of SRF. However, results only for MC, Ash and Total [Cl] are included since ToS considers the analyte (e.g SRF property) as a contaminant, whereas NCV and combustion behaviour (TG-DTG critical points) are not. The concentration and density of the analyte (**Eq. 2-5**) are required for the calculation of mineralogical factor, c , while NCV and critical TG-DTG points cannot be expressed neither as a fraction in the *lot* nor as an ingredient with density.

4.2.8.3 Statistical analysis to quantify the sub-sampling uncertainty for TG-DTG in SRF

The uncertainty emerging from sub-sampling for TG-DTG analysis was calculated with two statistical approaches: i) applying nested-ANOVA to the 38 combustion characteristic points (S is included) to estimate the relative contribution of sub-sampling stages and the overall RSD for the determination of the most critical points of SRF thermal behaviour (analytical results of critical TG-DTG points that formed datasets for nested-ANOVA is not presented in the Thesis, but it is provided in the **Supporting Information (SI.1)**); and ii) calculating the pooled relative standard deviation derived from replicate measurements to estimate the RSD emerging from analytical stage (AE) of entire TG-DTG signal.

- i) The obtainment of 37 combustion characteristic points resulted in a large set of variables (**Table 4-5**). Therefore these points were clustered into groups creating a smaller dataset easy to visualise and examine the correlation between them using the advanced statistical technique of principal components analysis (PCA) (Minoglou and Komilis, 2018). PCA is a dimensionality-reduction method that groups correlated variables into principal components (PCs) capturing the greatest part of variation of the initial set of variables (Minoglou and Komilis, 2018) – 37 combustion

characteristic points. Combustibility index, S, was not included in PCA as it is a factor calculated from TG-DTG signal and does not represent a point of this signal (**Eq. 4-3**). Before the use of PCA, data normalisation was performed since PCA tends to capture variables, which are on different scale here (**Table 4-5**), with the higher variances. Another key requirement was to detect the presence of outliers, in which PCA is highly sensitive (Serneels and Verdonck, 2008), by generating control charts (**Appendix E1**). PCA included: a scree plot that identified the number of PCs constituting the groups of variables along with the amount of variation captured; and loading scatter plots that show the correlation between variables and PCs. Based on Kaiser criterion, PCs with eigenvalues higher than one can be retrieved, but this approach is quite improvised (Braeken and Van Assen, 2017). Herein, the number of PCs was selected by checking the loading plots (Figure 5-19). As a rule of thumb, variables with loading ≥ 0.60 are sufficiently correlated with the corresponding PC and therefore they can be grouped into it (Minoglou and Komilis, 2018). Following the results of PCA, the variance of the combustion characteristic points was quantified at each stage of the sub-sampling process (**Figure 4-5**) through the variance of components obtained from the nested-ANOVA.

It was calculated the uncertainty of analytical stage emerging from sub-sampling of test sub-sample to test portion combined with sensitivity of TGA apparatus (AE) and the uncertainty of all riffle splitting and shredding stages from initial sample to test sub-sample (SE). The uncertainty arising from each stage of sub-sampling was not provided in the chapter of the Results for reasons of simplicity, but the results are given in **Appendix E4**. The relative contributions of AE and SE to total RSD were also calculated.

ii) Pooled RSD was calculated as follows:

$$\%RSD_{pooled} = \sqrt{\frac{RSD_1^2 + RSD_2^2 + \dots + RSD_k^2}{k}} \quad \text{Eq. 4-5}$$

RSD_{pooled} was calculated for: i) each test sub-sample providing evidence on AE of entire TG-DTG signal ($k = 10,442$) – RSD_i was the relative standard deviation of replicate measurements at each point; and ii) all test sub-samples of both designs providing a weighted average of AE of

TG-DTG signal ($k = 16$ from Gross_nested and 8 for Intra_nested) – RSD_i was the pooled relative standard deviation of each test sub-sample.

The reason that only AE was calculated for the entire TG-DTG signal was that nested-ANOVA would be impossible to be conducted 10,442 times for each point. In addition, the use of PCA to 10,442 variables would give a reduced number of new composite variables difficult to interpret and handle (Curuksu, 2018; Björklund, 2019).

Finally, the pooled RSD (**Eq. 4-5**) was calculated for each PC, TGA points, DTG points, and for the 38 combustion characteristic points (S is included) along with the respective relative contributions of AE and SE to determine the weighted average uncertainty for characterization of SRF combustion behaviour. The relative contribution of AE to the RSD_{pooled} for TGA and DTG points along with the RSD_{pooled} of the entire TG-DTG signal (ii) provided insights into the overall RSD arising from sub-sampling for TG-DTG analysis of SRF using **Eq. 2-2**. Noted that PE and SE of **Eq. 2-2** are insolubly connected and therefore SE as defined here included both SE and PE. Therefore, the overall RSD for the entire TG-DTG signal was calculated as follows:

$$Overall\ RSD\ (\%) = \sqrt{AE^2 + (Relative\ contribution\ of\ SE) * Overall\ RSD^2} \quad \text{Eq. 4-6}$$

All above-mentioned statistical analysis was performed with TIBCO Statistica™ 13.3.0 software as well.

4.3 Design of experiment 2: model for composition identification of SRF

Herein, a DoE was developed to construct a model for composition identification of SRF based on its prevalent polymers (**Section 2.4.1.2**) through thermal and spectroscopic analytical techniques. The model was trained and cross-validated with a supervised ML algorithm – multivariate random forest (MRF) regression (more details in **Section 4.3.3.3**) – using a training dataset from synthetic mixtures that covered all potential combinations of SRF composition based on its prevalent components.

Despite cross-validation incorporated into the stage of model training, the model was validated using a hold-out dataset that consisted of mixtures from genuine waste items extracted from commercially

produced SRF samples with respect to the seven prevalent polymers. Hold-out validation was implemented to assess the model performance in real waste samples, where cross-contamination and impurities are present. Finally, the model was tested in a dataset of intact commercially produced SRF samples – without the isolation of items that represented prevalent SRF polymers – to verify the suitability of the model in genuine SRF samples. **Figure 4-6** illustrates the type of datasets used in training, validation and testing for model development.

At this stage, the main limitation was related to reliably assessing the model generalization regarding the identification of biopolymers (cellulose, xylan, and lignin) in waste-derived samples. This limitation is attributed to the use of typical reporting proportions of biopolymers (**Table 5-5**) as observed values of the hold-out validation set. However, the proportions of biomass waste items (wood and paper) were known, leading to an alternative solution. Specifically, prevalent polymers were grouped into biomass and fossil-based polymers creating binary mixtures with biomass and plastic fraction.

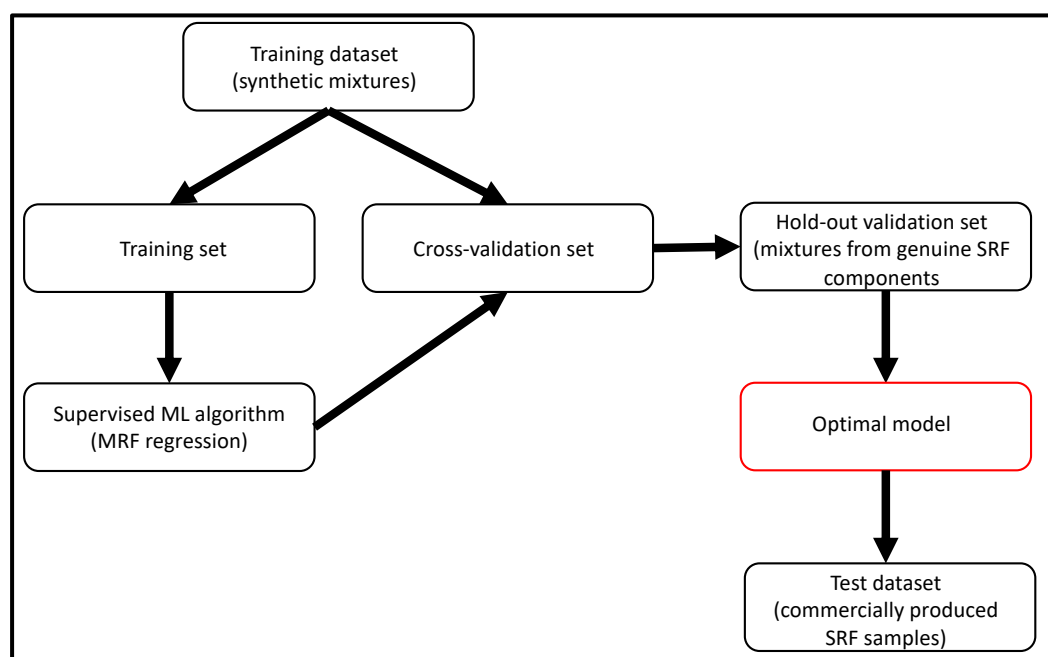


Figure 4-6. Type of datasets used in supervised ML algorithm to develop a model for composition identification of SRF based on prevalent polymers: i) training dataset derived from synthetic mixtures of artificially produced polymers that was used for model training (training set) including cross-validation (cross-validation set); ii) hold-out validation set derived from mixtures of genuine waste items extracted from commercially produced SRF samples for hold-out validation; and iii) test dataset derived from intact commercially produced SRF samples as received from MT/MBT plants for model testing.

Synthetic mixtures were prepared consisting of seven prevalent artificially produced polymers: cellulose, hemicellulose, lignin, PE, PP, PET, and PVC; able to resemble the typical composition of SRF following the principles of mixture design (Cornell, 2011). The composition of synthetic mixtures formulated the target region (design space) in which the model would be able to make predictions. Specifically, the upper and lower bounds of the seven polymers into the synthetic mixtures were defined by considering the findings from the second part of critical review (**Section 4.1.2.1**), while the obtainment and evaluation of the design space – number of mixtures and their composition – was carried out through a software dedicated to DoE including experiments with mixtures (Design-Expert V11). This matrix of synthetic mixtures constituted the output training dataset of the model.

Synthetic mixtures were subjected to TG-DTG and FTIR analytical techniques resulting in a big data matrix of analytical results that constituted the input training dataset of the model. The supervised ML algorithm (MRF regression) was applied since the traditional regression models were not able to deal with such complex and big datasets. The composition of mixtures in the hold-out validation set was defined by the design space, while the composition of SRF samples in the testing dataset was inspected through manual sorting to ascertain that it falls within the design space. **Figure 4-7** provides an overview of the methodological steps that I followed to construct the model.

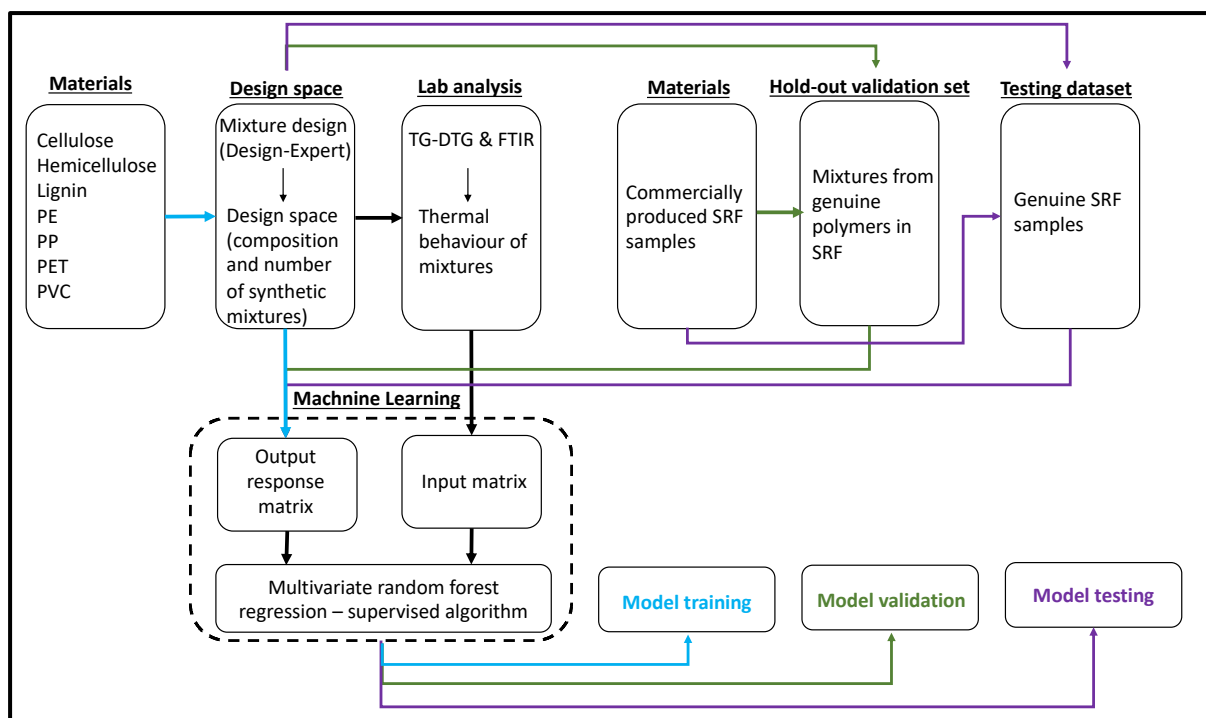


Figure 4-7. Methodological overview for DoE2 to address the research objective (O4): Development of a model for composition identification of SRF based on seven prevalent components: cellulose, hemicellulose, lignin, HDPE, PP, PET and PVC. DoE2 consisted of: i) materials including synthetic polymers for model training and commercially produced SRF samples for model validation and testing; ii) a mixture design that formulated the design space in which the model would make predictions – the range of proportions of these polymers into a typical SRF composition – with the help of Design-Expert software; iii) analytical techniques for the determination of thermal behaviour of the samples – analytical results represent the predictors of the model; and iv) a supervised ML algorithm (MRF regression) as a tool for model construction. Blue, green and purple lines denote the steps of model training, validation, and testing, respectively. Black lines indicate that the related steps are common for training, validation, and testing. Dotted black line indicates the process of ML data analysis.

4.3.1 Materials of DoE2

The materials used for DoE2 were microcrystalline powder cellulose (Sigma-Aldrich, UK), xylan from beechwood (Apollo Scientific, UK) as representative of hemicellulose (**Section 2.4.1.2**), kraft lignin (Sigma-Aldrich, UK), HDPE in pellet form (Sigma-Aldrich, UK) as representer of PE, isostatic PP in a pellet form (Sigma-Aldrich, UK), granular PET (Sigma-Aldrich, UK), and medium molecular weight PVC in powder form (Sigma-Aldrich, UK) as representer of CI in SRF. These materials were used for the design of response matrix for model training.

A typical SRF sample (ca. 2 kg) produced from residual MSW in a MT plant in the UK, processing a mixture of residual household MSW and commercial waste (corporate name withheld for confidentiality reasons), was obtained to extract waste items that would represent the prevalent

polymers in SRF for hold-out validation. Four typical SRF samples (ca. 0.8 kg) from two different MT plants in the UK, processing a mixture of residual household MSW and commercial waste were obtained to test the validity of the model in representative commercially produced SRF samples. Liquid nitrogen was also used, a reagent for the cryogenic shredding of SRF samples, components, and synthetic polymers.

4.3.2 Analytical techniques of DoE2

Two analytical techniques were applied to obtain the input datasets for model construction and therefore address the objectives of DoE2 methodological part:

I. Thermogravimetric analysis combined with the derivative of TGA signal (TG-DTG):

Similarly to DoE1 (**Section 4.2.7.2**), TG-DTG experiments were conducted also for the purpose of DoE2 under non-isothermal operating conditions: atmosphere of thermal decomposition: nitrogen; flow rate: 50 ml min⁻¹; heating rate: 10 °C min⁻¹; sample holder: alumina 150 µl; maximum temperature: 750 °C; test portion mass: 10 mg. These conditions were selected considering the literature findings obtained from the second part of critical review related to the typical operating conditions applied in TG-DTG experiments of waste-derived materials for compositional analysis purposes (**Section 2.4.1.2**). The main difference in TG-DTG conditions between DoE1 and DoE2 was that the inert atmosphere applied to the experiments of the latter. In DoE2, sample preparation processes applied to the samples of model training (synthetic mixtures), validation (waste mixtures) and testing (commercially produced SRF samples) were slightly different and therefore they were described separately in **Section 4.3.5.1**. The equipment, software, and process analysis used in TG-DTG experiments of DoE2 were identical to these of DoE1 (**Section 4.2.7.2**), while data handling and therefore obtainment of analytical results were different. In DoE2, only raw data of TG-signal and DTG-signal were obtained by the software (STAR[®]) resulting in two different datasets provided in excel files. TG-signal provided 4321 points of weight loss (% w/w) per second from each measurement and DTG-signal provided 4321 points of rate of weight loss (% w/w min⁻¹) per second from each measurement. The average of three replicate measurements was

taken for each test sample. Further processing techniques were applied to raw experimental data discussed on **Section 4.3.5.2**.

II. Fourier transform infrared spectroscopy (FTIR): FTIR analysis, widely used for qualitative analysis of polymer materials, was used to determine the infrared region of the electromagnetic radiation spectrum of test samples. FTIR spectra were recorded on an IR spectrometer using attenuated total reflectance (Spectrum Two™ Universal ATR, PerkinElmer) at a resolution of 4 cm^{-1} for 32 scans in the range of 4000-400 cm^{-1} . Similar settings were found in related studies that applied FTIR to waste-derived materials (Moreno and Font, 2015; Asadieraghi and Daud, 2014; Barontini et al., 2015; Ducom et al., 2020; Ma et al., 2019; Chhabra et al., 2019). Small quantities of test portions (ca. 20-30 mg) were placed onto the diamond crystal using the pressure arm to ensure a good contact of the sample with the crystal. IR radiation passed through the sample leading to the absorbance of some radiation by the sample, while some radiation was transmitted. The resulting signal given by the detector provided a spectra in a molecular fingerprinting region (Sim et al., 2014). Instrument settings, starting sample analysis, data handling and obtainment of analytical results were accomplished using the PerkinElmer Spectrum™ 10 software (PerkinElmer, 2021). Herein, raw analytical results were obtained providing 3601 points of absorbance per wavelength from each measurement. Three replicate measurements were taken for each test sample.

III. Total chlorine concentration (Total [Cl]): Similarly to DoE1 (**Section 4.2.7.2**), Cl measurements were taken in DoE2. Specifically, Total [Cl] was determined in the hold-out validation samples, expressed in % w/w as received basis (% w/w), measured through the combined standard method BC (BS EN 15400, 2011) and photometric method of Palintest Chloridol test (Palintest-Test instructions, 2019).

Noted that the combination of TG-DTG and FTIR did not constitute an EGA technique, since TG-DTG and FTIR instruments were not coupled and therefore FTIR did not analyse the evolved gas products of the sample produced during TG-DTG. Analytical results of TG-DTG and FTIR for synthetic mixtures (training set), waste mixtures (hold-out validation set), and commercially produced

SRF samples (testing set) are not presented in this Thesis, but they are provided in the **Supporting Information (SI.2)**.

4.3.3 Model design tools of DoE2

A basic knowledge background is provided in this section related to statistical tools and experimental designs selected to synthesize this methodological part. The notion of experiments with mixtures (or mixture design) is presented. An introduction to ML algorithms is following along with the mechanism of multivariate random forest (MRF) regression, a ML algorithm used to build the predicted model.

4.3.3.1 Experiments with mixtures

In mixture experiments or experiments with mixtures, the related DoE factors refer to the components of the mixture and therefore their levels are not independent (Montgomery, 2017). Mixture experiments constitute a special case of response surface experiments, in which response variable is dependent on the proportions of the components (Oehlert, 2010). In mixture experiments, there are two principal restrictions (Cornell, 2011): the equality constraint (**Eq. 4-7**) and the non-negativity constraint (**Eq. 4-8**)

$$\sum_{i=1}^q X_i = 1 \quad \text{Eq. 4-7}$$

$$X_i \geq 0 \quad i = 1, 2, \dots, q \quad \text{Eq. 4-8}$$

where, q is the number of components ($q = 7$) and X_i is the proportion of i component in the mixture.

This design space is called a simplex in q dimensions. An ordered arrangement consisting of a uniformly spaced distribution of points on a simplex is known as a lattice (Cornell, 2011). For example the simplex space with three components is an equilateral triangle and, with four components is tetrahedron. A $\{q, m\}$ simplex-lattice design for q components consists of design points on the

simplex where the proportions of each component take the $m+1$ equally spaced values from 0 to 1 as follows (Montgomery, 2017):

$$X_i = 0, \frac{1}{m}, \frac{2}{m}, \dots, 1 \quad \text{Eq. 4-9}$$

For example, the {3, 2} simplex lattice consists of the six design points (1, 0, 0), (0, 1, 0), (0, 0, 1), (1/2, 1/2, 0), (1/2, 0, 1/2), and (0, 1/2, 1/2) (Oehlert, 2010). The number of design points in the {q, m} simplex-lattice design, which corresponds to the number of synthetic mixtures in this study, is defined as:

$$N_p = \frac{(q + m - 1)!}{m! (q - 1)!} \quad \text{Eq. 4-10}$$

The lattice corresponds to a specific polynomial equation of degree m in q components. For example, when the order m is equal to one, the relationship between the components and response variables is linear (no interaction effects occur). For m equal to two, the relationship is not linear and interaction effects occur between two components and the model is quadratic. It should be mentioned that in terms of regression, the model will be linear but the quadratic term will be added in the model $(\sum_i^q \sum_j^q \beta_{ij} x_i x_j)$, indicating a synergistic or antagonistic blending. For m equal to 3 the model is cubic considering the interaction effects among up to three components, whereas m equal to four includes also the potential interaction among up to four components (quartic model). **Figure 4-5** presents two common examples of simplex lattice designs. Further discussion on the polynomials employed in experiments with mixtures is reported elsewhere (Cornell, 2011; Oehlert, 2010).

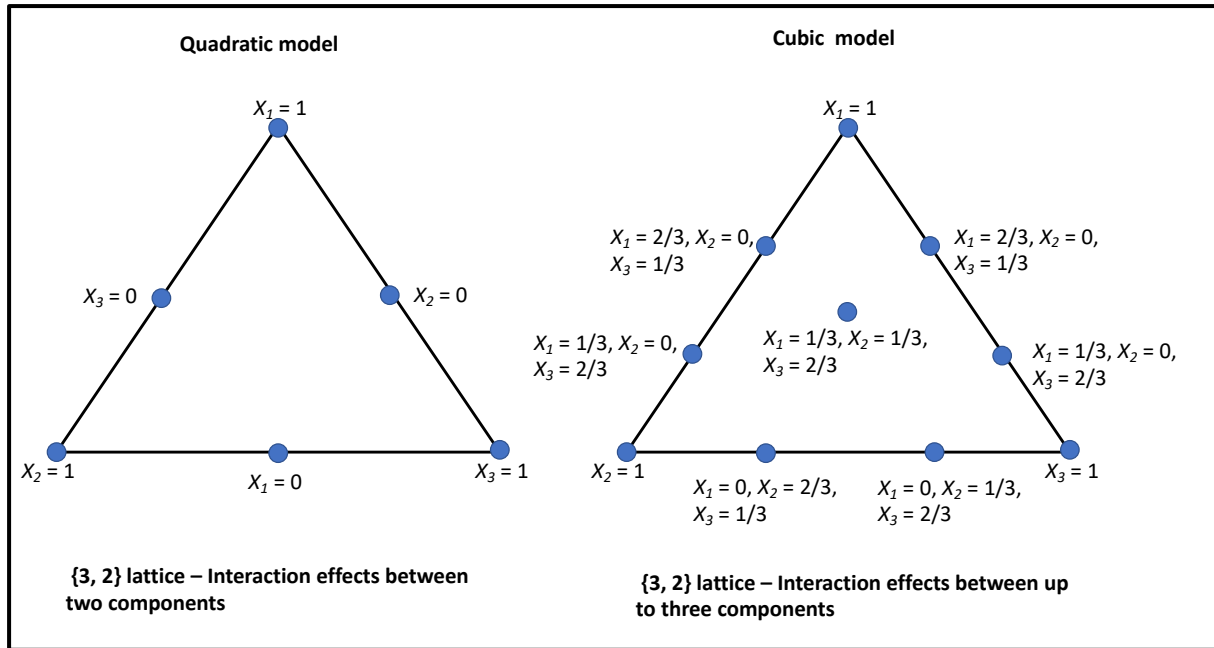


Figure 4-8. Simplex lattice designs for $q = 3$ with two different orders: $m = 2$ and $m = 3$ providing the design points that will constitute the design region. Adapted by Montgomery (2017).

However, in realistic mixture problems the components usually have both lower and upper bound constraints resulting in an irregular design region that is no longer simplex (Montgomery, 2017). In such cases, the mixture design is not only based on the equality constraint (Eq. 4-7), but also to other more complex constraints. Mixture designs can be adapted to such issues with the introduction of pseudo-components and use of special software, often referred as computer-generated optimal designs (Montgomery, 2017). These designs are called optimal in the sense of minimizing the estimation variance with a minimum number of runs (Oehlert, 2010).

There is a wide variety of optimality criteria with the most popular in mixture experiments being the D-optimal and I-optimal design (Montgomery, 2017). D-optimality seeks to minimise the volume of the joint confidence region of the regression coefficients by maximising the determinant of the $X'X$ matrix (Montgomery, 2017). It produces designs that best estimate the effects of the factors, which is particularly suited for screening studies (Stat-Ease, 2019). I-optimality criterion picks points that minimize the integral of the prediction variance across the design space (Goos et al., 2016). It produces designs that provide lower average prediction variance across the experimentation region (Stat-Ease, 2019). I-optimal designs are selected when prediction is important (Stat-Ease, 2019). A detailed explanation of optimal designs can be found elsewhere (de Aguiar et al., 1995; Mancenido et

al., 2019; Goos et al., 2016; Cook and Nachtrheim, 1980). Herein, it was not provided any mathematical description of the optimal designs since the efficiency of optimal designs in terms of the best possible design is evaluated by the related DoE software (e.g. Design-Expert) (Montgomery, 2017).

4.3.3.2 *Machine learning (ML) algorithms*

Machine learning, a field built upon statistics, constitutes an application of artificial intelligence (Pezzè and Zhang, 2014) that provides generalizable predictive patterns with minimum human intervention for real-world data (Bzdok et al., 2018). A ML model is built through training (or calibration) and validation. The training set is the subsection of a dataset from which the ML algorithm “learns” relationships between the features and the target variable – fits the model, while the validation set is another subset of the input data from which the ML algorithm identifies relationships between the known outcomes for the target variable and the features of the validation set – qualifies the model performance. After training and validation, testing might be applied by selecting a separate input dataset that provides a final estimate of the performance of ML model. However, testing dataset should never be used to make decisions about which algorithms to use or for improving algorithms. Partitioning data into training, validation, and testing are able to create highly accurate model providing a real sense of prediction outcomes and therefore confidence in model accuracy.

ML is suitable for complex tasks that are extremely hard to program by hand (Lison, 2015), such as dealing with ‘wide data’ where the number of input variables exceeds the number of observations/samples (Bzdok et al., 2018). Despite that, ML models can improve their prediction accuracy and therefore their experience over time by increasing the amount of data that are processed (Lison, 2015). This advantage of ML to adapt to new situations offers the opportunity to include future research data in an existing ML model resulting in a better decision making. In addition, ML is able to accurately identify trends making minimal assumptions about the collected data systems, even under a not well experimental design (Bzdok et al., 2018).

There is a wide variety of ML algorithms and techniques that are used to design a model depending on the type of data available to be processed (Lison, 2015). Herein, a basic description of the main types of ML algorithms is provided:

- i. Supervised learning, is used when a set of both response and input variables is given (Lison, 2015). Supervised learning classified into regression and classification algorithms (Tyralis et al., 2019) is suitable for the design of predicted models. Popular, ML techniques based on supervised learning are regression, decision trees, random forests, logistic regression, and k-nearest neighbors (Kubat, 2017). An explicit description of supervised ML algorithms and techniques is reported by Kubat (2017);
- ii. Unsupervised learning is used when only the set of input variables is available (Lison, 2015). Unsupervised learning is suitable for clustering population. Popular, ML techniques based on unsupervised learning are Apriori algorithms and K-means; and
- iii. Reinforcement learning is used when no access to the output set is available, but a measure of the quality of the output following the input set is obtained (Lison, 2015). Reinforcement learning is suitable for specific decision making. A popular ML technique is Markov decision process.

4.3.3.3 *Multivariate random forest (MRF) regression*

Random forest used in supervised learning is a versatile and accurate classification and regression technique providing interpretable outputs for wide classes of problem (Segal and Xiao, 2011).

Random forest is a non-parametric model and therefore distribution assumptions are not required (Quan and Valdez, 2018). Random forest is a tree-structured method that subdivides data into more homogeneous sub-groups with respect to both predictors and response (Segal and Xiao, 2011). For continuous responses, the terminal subgroup summaries – typically means – represent the predictions (Segal and Xiao, 2011).

Random forest is a modification of bagging, which is an ensemble algorithm that builds a number of de-correlated trees and averages them aiming to reduce the variance (or minimize overfitting)

(Boehmke and Greenwell, 2019). By applying the bagging algorithm, each tree is designed from a bootstrap sample obtained with replacement by the training data resulting in different trees (Segal and Xiao, 2011). In random forest regression, bagging via bootstrap resampling is combined with further injection of randomness (Segal and Xiao, 2011). In bootstrap resampling of random forest, the $\approx 1/3$ of the observations, termed out-of-bag (OOB), omitted from each bootstrap sample serving as test data for tree construction using that sample (Segal and Xiao, 2011). In other words, each individual tree uses $\approx 1/3$ of the observations to build the tree, while the remaining observations OOB are used to evaluate the prediction accuracy of the tree (González et al., 2016). Instead of determining the optimal subdivision of a tree member by evaluating all allowable partitions on all predictors, as occurs in bagging, a random subset of features is drawn (Segal and Xiao, 2011). The size of this random subset, called *mtry*, designates the number of predictors as candidates for splitting which is the most critical tuning parameter for the forest procedure (Xiao and Segal, 2009; Janitza and Hornung, 2018; González et al., 2016). Bagging is a special case of random forest when *mtry* is equal to the number of predictors (Liaw and Wiener, 2002). MRF is constructed by generating an ensemble of multivariate regression trees (MRTs) via bootstrap resampling and predictors subsampling similarly to univariate random forest (Quan and Valdez, 2018).

The framework of regression tree was set by Breiman et al. (1984) including four components: i) a set of binary (yes/no) questions to split the predictor space into sub-groups, which are called nodes. By starting with a single node that includes all data at the top of the tree, the tree is grown by repeated splitting of the data forming two nodes at each stage (De'Ath, 2002). The terminal nodes that do not have any descendant nodes is called leaf; ii) a measure of the homogeneity at each node, known as impurity measure, which is defined as the total sum of squares (SS) of the response variable values about the node mean (De'Ath, 2002); iii) a split function, $\phi(s, t)$, that can be evaluated for each split s , of each node t via the impurity measure; and iv) a means for determining the appropriate tree size (Segal and Xiao, 2011). Details on how to construct a random forest as given by Linusson (2013).

In the single (univariate) response setting, y_i and $x_{i,j}$ ($i = 1, \dots, n$; $j = 1, \dots, p$) constitute the response and predictors, respectively (Segal and Xiao, 2011). A node t that contains a group of cases is split into

two child nodes, a ‘left’ node t_L , and a ‘right’ node t_R (Segal and Xiao, 2011). The corresponding split function is formed as follows (Segal and Xiao, 2011):

$$\varphi(s, t) = SS_{(t)} - SS_{(t_L)} - SS_{(t_R)} \quad \text{Eq. 4-11}$$

In multiple response data using MRT, $y_{i,k}$ ($i = 1, \dots, n$; $k = 1, \dots, m$) and $x_{i,j}$ ($i = 1, \dots, n$; $j = 1, \dots, p$) constitute responses and predictors, respectively (Segal and Xiao, 2011). MRT is an extension of the univariate case, where all responses are analysed simultaneously considering anticipated dependencies between responses (Quan and Valdez, 2018). To extend univariate to multivariate regression trees, the split function is modified by replacing the impurity measure with a ‘covariance’ weighted analog, as follows (Segal and Xiao, 2011; Quan and Valdez, 2018):

$$SS(t) = \sum (y_i - \mu(t)) V^{-1}(t, \eta) (y_i - \mu(t)) \quad \text{Eq. 4-12}$$

Where V^{-1} represents the covariance matrix of the multivariate response variable, η represents parameters characterizing prescribed covariance structures (e.g., auto regressive, compound symmetry). By applying **Eq. 4-12** to **Eq. 4-11** a multi-response split function is generated (Segal and Xiao, 2011). The difference between univariate and multivariate random tree is that the $SS(t)$, which is called node cost (Haider et al., 2015), is measured as the sum of squares of the Mahalanobis distance to capture the correlations in the data in MRT, whereas node cost is measured as the sum of Euclidean distance square in the univariate case (Rahman, 2017). Mahalanobis Distance captures the distance of the sample point from the mean of the node along the principal component axes (Rahman, 2017).

For a successfully training of tree-based model, the model complexity should be controlled by keeping a balance between bias and variance leading to the maximum prediction accuracy (Quan and Valdez, 2018). A poor model performance may cause: i) overfitting – captures the noise along with the underlying pattern in data resulting in inability to generalise to new data due to excessively model complexity – leading to high variance and low bias; or ii) underfitting – inability to capture the underlying trend of data due to excessively model simplicity – leading to low variance and high bias (Hastie et al., 2009). Overfitting (residual correlation) is likely to occur especially when the number of

predictors is increased (Rahman et al., 2017). In MRF regression, on the one hand trees need to grow at maximal depth for low prediction error (bias), on the other hand the correlation between residuals of different tree members of the forest should be kept low for unbiased prediction error (variance). In case of high residual correlation, randomization by pre-specifying $m \ll p$ is needed (Segal and Xiao, 2011).

So far, very limited research can be found in MRF, mainly in ecology with a focus on: evaluation of the changes of estuarine community composition along landscape structures (Miller et al., 2014); and relationships between spider species with environmental characteristics (Segal and Xiao, 2011).

Before MRF, MRT regression was applied for modelling species-environmental relationships (De'Ath, 2002; Ruppert et al., 2010). A recent extension of MRF regression for integrating drug response predictors from a variety of genomic characteristics was proposed by Rahman et al. (2017). This extended algorithm, called integrated MRF, provided an integrated prediction from different data subtypes using MRF (Rahman et al., 2017). This package ('IntegratedMRF') could be selected instead of 'Multivariate_Random_Forest' and therefore the best dataset combination could be selected by the machine. However, the very limited technical information and the increased computer processing power required led to choose 'Multivariate_Random_Forest'.

4.3.4 Formulation of optimal mixture design space

The first step of model construction was to define a well-designed model region able to represent the typical composition of SRF based on its prevalent polymers. This was the most critical step of modeling as the design region would delimitate the range in which the model would make predictions. The design space was defined by the number of components that represented the number of materials identified in a mixture, the number of design points representing the population of mixtures consisting of the selected components, and the position of the design points that represented the composition of mixtures. To achieve this, a series of empirical actions were taken with the use of the dedicated software to mixture design, Design-Expert V11. With this software, the process to define the design space was quite automated and effortless.

Specifically, I had to define specific parameters including the type of mixture design (*optimal*), the number of components ($q=7$), the complex constraints, the exchange algorithm (*Best Exchange* algorithm), the optimality criterion (I-optimality), and the parameters for evaluation of the design space with the fraction design space (FDS) plot. An overview of the process for the formulation of the mixture design space with a goal to represent the typical composition of SRF based on its prevalent components is presented in **Figure 4-9**.

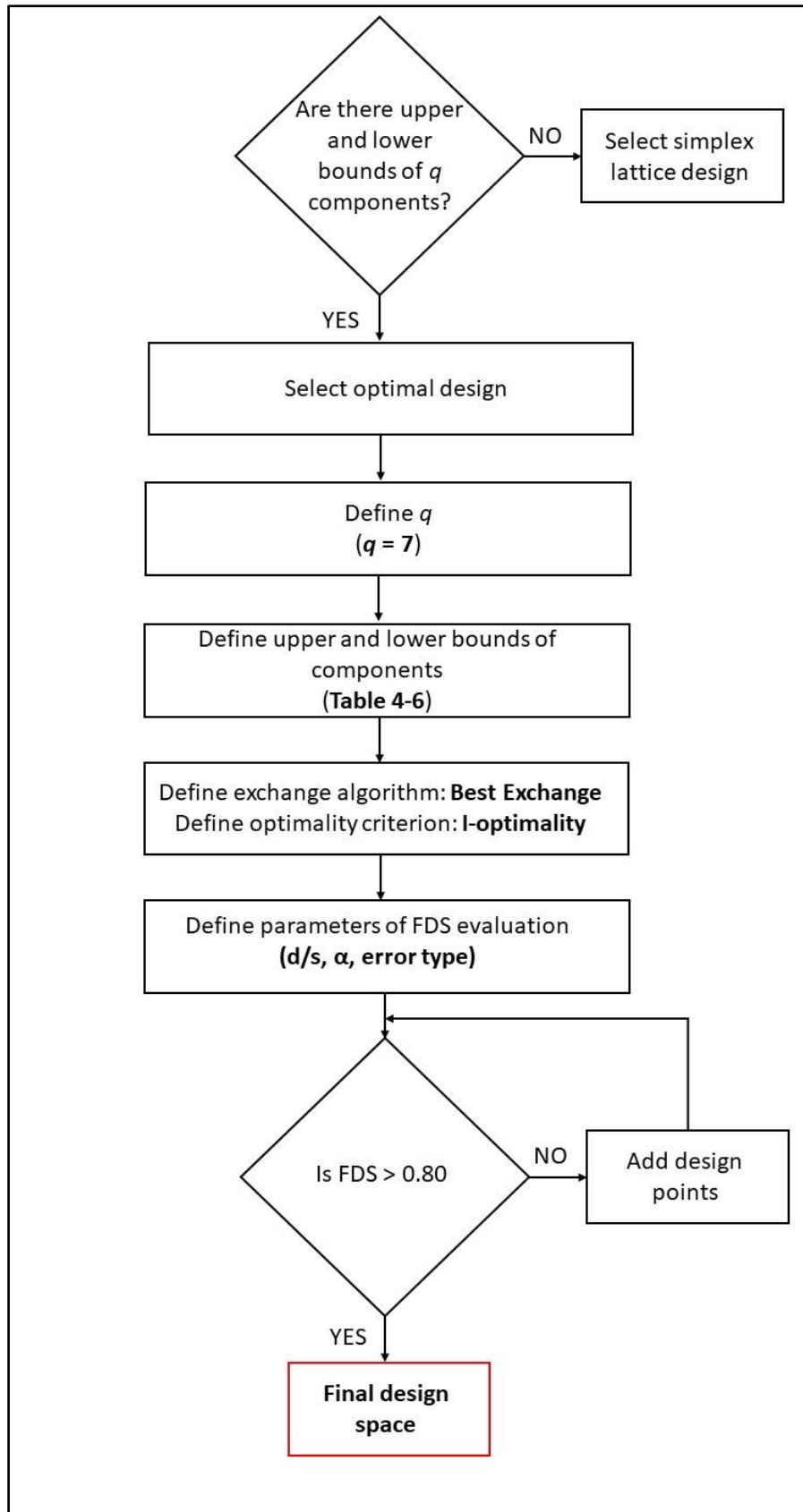


Figure 4-9. Overview of empirical actions taken to formulate a design space that would represent the typical composition of SRF based on its prevalent components using the dedicated software to mixture designs, Design-Expert.

Type of mixture design: A simple approach to define the design space would be to select a simplex lattice design (no existence of complex constraints) for the seven prevalent SRF polymers resulting in a heptahedron where the proportions of these components would range from 0 to 1. In that case, the design region would be relatively wide necessitating an overwhelming number of mixtures to obtain sufficient prediction accuracy. The smaller the mixture design space, the better the prediction accuracy of a model for a specific number of mixtures (Anderson et al., 2018). Besides, a simplex lattice design that considers only the equality criterion is not suitable to depict the composition of SRF. For example, a design point that corresponds to a pure mixture that contains only cellulose ($x_1 = 1$ from **Eq. 4-7**) is not able to represent SRF composition – there is not SRF consisting only of cellulose. The ranges of polymer proportions in SRF are different and therefore the addition of complex constraints is necessary. Thus, an optimal mixture design was selected and the related required parameters were introduced in the software, presented below:

Number of components, q : The number of components was set at seven ($q = 7$): cellulose ($i = 1$); xylan as representative of hemicellulose ($i = 2$); lignin ($i = 3$); HDPE as representative of PE ($i = 4$); PP ($i = 5$); PET ($i = 6$); and PVC as representative of Cl in SRF ($i = 7$), which are the most prevalent polymers identified in SRF as reported in the literature (**Section 2.4.1.2**).

Design order, m : I selected quadratic order ($m = 2$) considering the existence of potential interaction effect between two components (**Section 2.4.2.2-c**).

Complex constraints: At this stage, multiple complex constraints were added to set the upper and lower bounds of the seven components creating a design space that simulates SRF composition based on its prevalent polymers. The design space was a complex irregular region with seven sides (for $q = 7$) that were formed from typical ranges of weight percentages of the seven polymers in SRF. By that, the design space covered all potential combinations of components in the mixtures that can be identified in commercially produced SRF samples. Specifically, it was specified: i) the minimum and maximum weight percentages of biomass and plastic fraction that can be found in typical SRF samples considering the literature evidence presented in **Table 2-3**. It was assumed that biomass consisted only of cellulose, hemicellulose and lignin, while plastic fraction consisted only of PE, PP,

PET and PVC; ii) the minimum and maximum ratio of different combination of biopolymers (e.g. cellulose: hemicellulose, cellulose: lignin, and lignin: hemicellulose) obtained from critical review analysis related to the weight percentage participation of biopolymers in SRF (**Figure 5-3**); iii) the minimum and maximum ratio of different combination of plastic polymers (e.g. PE: PP and PE: PET) obtained from critical review analysis (**Figure 5-4**); and iv) the percentage participation of PVC so that the design space consisting of simulated SRF samples (synthetic mixtures) classified from Class code 1 ($\leq 0.2\%$ w/w_d) to Class code 4 ($\leq 1.5\%$ w/w_d) for Total [Cl]. **Table 4-6** illustrates the eight complex constraints along with the considered literature evidence and the related assumptions that were taken.

Table 4-6. Eight complex constraints added in the mixture design to delimit the design space according to the minimum and maximum percentage participation of seven prevalent polymers that can be potentially identified in typical commercially produced SRF samples (**A:** cellulose, **B:** hemicellulose, **C:** lignin, **D:** PE, **E:** PP, **F:** PET, **G:** PCV) as received reporting basis.

No	Complex constraint	Literature evidence	Assumption	Reference
1	$0.30 \leq A + B + C \leq 0.90$	Minimum: <i>Paper/cardboard & Wood</i> = 11% w/w for a reported SRF composition with 59% w/w unidentified materials and 9% w/w <i>Textiles</i> Maximum: <i>Paper/cardboard & Textiles</i> = 87% w/w	At least 30% w/w of unidentified materials and <i>Textiles</i> contain biomass leading to a total 31% w/w of biomass fraction in SRF. <i>Textile</i> waste category consists only of natural fibers	Table 2-3, (Sarc et al., 2019) Table 2-3, (Wagland et al., 2011)
2	$0.10 \leq D + E + F + G \leq 0.70$	Minimum: <i>Plastics</i> = 11% w/w Maximum: <i>Plastics & Textiles</i> = 60% w/w	Considering this value with a safety factor 15% <i>Textile</i> waste category consists only of synthetic fibers	Table 2-3, (Wagland et al., 2011) Table 2-3, (DEFRA, 2014)
3		Minimum: the ratio of LCI of cellulose (44.4% w/w) and UCI of hemicellulose (28.5% w/w) found in <i>Wood</i> was equal to 1.6	Biomass fraction in SRF consists mainly of <i>Wood</i>	Section 5.2

No	Complex constraint	Literature evidence	Assumption	Reference
4	$1.30 \leq A/B \leq 10.00$	Maximum: the ratio of UCI of Biomass fraction in SRF cellulose (84.1% w/w) and LCI of hemicellulose (7.8% w/w) found in <i>Natural fibers</i> was equal to 10.8	Biomass fraction in SRF consists mainly of <i>Natural textiles</i>	Section 5.2
	$1.30 \leq A/C \leq 4.00$	Minimum: the ratio of LCI of cellulose (44.4% w/w) and UCI of lignin (26.9% w/w) found in <i>Wood</i> was equal to 1.7	Biomass fraction in SRF consists mainly of <i>Wood</i>	Section 5.2
		Maximum: Typical composition of cellulose and lignin in SRF produced from MSW was 61.1% w/w and 31.2% w/w, respectively resulting in a ratio 2	The value of the ratio was doubled. The confidence intervals of lignin in the different biomass waste categories were too wide to use them for this constraint.	(Conesa and Rey, 2015)
	$0.50 \leq C/B \leq 5.00$	Minimum: the ratio of LCI of lignin (0.8% w/w) and UCI of hemicellulose (19.6% w/w) found in <i>Natural fibers</i> was equal to 0.05	The value of this ratio was extremely small coming from specific materials that do not contain lignin at all. Yet in most biomass materials lignin and hemicellulose content ranges in similar levels.	Section 5.2
5		Maximum: Typical composition of lignin and hemicellulose in SRF produced from MSW was 31.3% w/w and 7.6% w/w, respectively resulting in a ratio 4.	The ratio was kept with a safety factor 25%	(Conesa and Rey, 2015)
6	$0.80 \leq D/E \leq 3.00$	Minimum: the ratio of LCI of PE (32% w/w) and UCI of PP (22% w/w) was equal to 1.6	A ratio < 1 was selected to cover a rare case that SRF might contain more PP than PE	Section 5.2
		Maximum: the ratio of UCI of PE (43% w/w) and LCI of PP (17% w/w) was equal to 2.5	The ratio was kept with a safety factor 20%	Section 5.2

No	Complex constraint	Literature evidence	Assumption	Reference
7	$2.00 \leq D/F \leq 6.00$	Minimum: the ratio of LCI of PE (32% w/w) and UCI of PET (13% w/w) was equal to 2.4	The ratio was kept with a safety factor 15%	Section 5.2
		Maximum: the ratio of UCI of PE (43% w/w) and LCI of PET (8% w/w) was equal to 5.3	The ratio was kept with a safety factor 15%	Section 5.2
8	$0.003 \leq G \leq 0.03$	PVC is selected in synthetic mixtures as an exclusive source of Cl	PVC with Total [Cl] 53.7% w/w was used to create mixtures with Total [Cl] ranging from 0.15 (Class code 1) to 1.60% w/w (Class code 4).	Table 2-1

By introducing these complex constraints from **Table 4-6**, the software returned the upper and lower bound constraints of each component (**Table 4-7**) that eventually defined the ranges of the proportion of each component in the mixtures simulating every potential combination of polymer proportions identified in SRF. Noted that the optimal mixture design considered the upper and lower bounds along with the equality constraint to provide the composition of the mixtures ($\sum_{i=1}^7 x_i = 1$).

Table 4-7. Ultimate upper and lower bound constraints of seven components simulating the ranges of prevalent SRF polymers in commercially produced samples given by Design-Expert software taking into account the introduced complex constraints, indicating the design space in which prediction would be taken.

Letter	Component	Lower bound	Upper bound
A	Cellulose	0.205	0.655
B	Hemicellulose	0.026	0.133
C	Lignin	0.051	0.354
D	PE	0.033	0.390
E	PP	0.030	0.262
F	PET	0.010	0.140
G	PVC	0.003	0.030

Exchange algorithm: This parameter refers to the algorithm that constructs the design region by searching over a discrete grid of possible design points (Goos and Jones, 2011). Exchange algorithm provides the proportions of components in the mixtures. Three main options were provided including *Point Exchange*, *Coordinate Exchange*, and *Best Exchange*. *Point Exchange* searches for a geometric set of candidates, while *Coordinate Exchange* algorithm searches for a free candidate set resulting in random design points that located anywhere in the design space. *Best Exchange* algorithm uses *Point Exchange* for half of the design points and *Coordinate Exchange* for the other half, which is also the most recommended (Stat-Ease, 2019). All exchange algorithms under constant optimality criteria were checked and the *Best Exchange* algorithm was selected.

Optimality criterion (Montgomery, 2017): Three main optimality criteria are provided including D-, I- and A- optimal designs. The selection of the best criterion depends on the purpose of design. I-optimality criterion is recommended for predicted models (Stat-Ease, 2019). All optimality criteria were checked under constant exchange algorithms and I-optimality criterion was selected.

Evaluation of the design space: The adequacy of the design space specified by the above-mentioned parameters was evaluated via the FSD plot that provides the area or volume of the design region that can estimate under a specific level of precision (Stat-Ease, 2019). The ratio of this volume to the total volume of the design space is the called fraction of the design space (Whitcomb, 2008). FDS plot shows the cumulative fraction of the design space on x-axis against a standard error on the y-axis (Whitcomb, 2008). In practice, FDS plot helps to determine the number of mixtures and assess the sizing of experiments with mixtures before experiments is performed. An FDS greater than 0.80 is generally acceptable to ensure that the majority of the design space is precise enough for our purpose (Whitcomb, 2008). If it is less than 0.80, it is recommended to add more design points (mixtures) (Stat-Ease, 2019).

To obtain the FDS graph, the following factors need to be defined by the end-user (Stat-Ease, 2019):

- Signal (d): the important change (Δy) to detect each response;
- Noise (s): the experimental error for each response;

- Type of error under a certain level of significance (α) including: i) “mean”, the half-width of the confidence interval, used when the goal of the experiment is to optimize responses using the model calculated during analysis; ii) “prediction”, the half-width of the prediction interval, used when the goal is to verify individual outcomes; iii) “tolerance”, the half-width of the tolerance interval, useful for setting specifications based on the experiment; and iv) “difference”, minimum change in the response that is important to detect, used when searching for any change in the response.

It should be noted that the evaluation of the design space in Design-Expert considers that the mixture matrix – design space – is the input dataset of the model (X matrix) and the parameters defined in FDS plot related to the response variables (Y matrix). However, this research aims to reverse the design space into an output matrix and apply a ML algorithm instead. This novel action was done for two main reasons: i) to deal with the big data matrix of analytical results – 3601 variables from FTIR and 4321 variables from each TG- and DTG- thermogram – making the use of the traditional linear regression modelling offered by the Design-Expert unsuitable; and ii) to create a model tool that would predict the composition of the mixture using the analytical results from thermal and spectroscopic techniques.

In model evaluation through the FDS plot, some hypothetical values were supplied to the required parameters assuming that the model space is the X matrix of the linear regression. It was quite complex and time consuming to identify the signal to noise ratio (d/s) for such a wide matrix of analytical results. Besides, FDS evaluation was step prior experimentation and therefore the related factors were specified approximately based on previous experience or pre-experimental analytical results. Insights into this ratio were gained by calculating the ratio of the standard deviation of analytical results between two synthetic mixtures to the standard deviation of their replicates.

Synthetic mixtures were prepared to calculate the CI recovery in **Section 4.2.5**. This ratio gave a value equal to 1.3, which was selected as signal to noise ratio. Finally, a “mean” error type was selected under 0.05 significance level.

Multiple optimal designs were executed for a {7, 2} optimal mixture design under different combinations of design (exchange algorithm and optimality-criterion) and evaluation parameters (signal-to-noise ratio and type of error). By default, the best design combination (*Best Exchange* algorithm and I-optimal criterion) returned 42 design points including three replicates as a minimum number of mixtures with FDS 0.81. The design points were increased up to 53 by adding 11 more mixtures, from which two mixtures were replicates, so that to obtain an FDS equal to 0.90 (**Figure 4-10**) – higher than the recommended value of 0.8 (Stat-Ease, 2019).

Five replicates were added to examine the pure error and help the ML algorithm (MRF regression) to reduce the prediction error. Replicate design points are different from the replicate measurements. Replicate points are mixture samples with identical composition that were prepared under the same process. Replicate design points are test samples, while replicate measurements are test portions – the same mixture with multiple analysis.

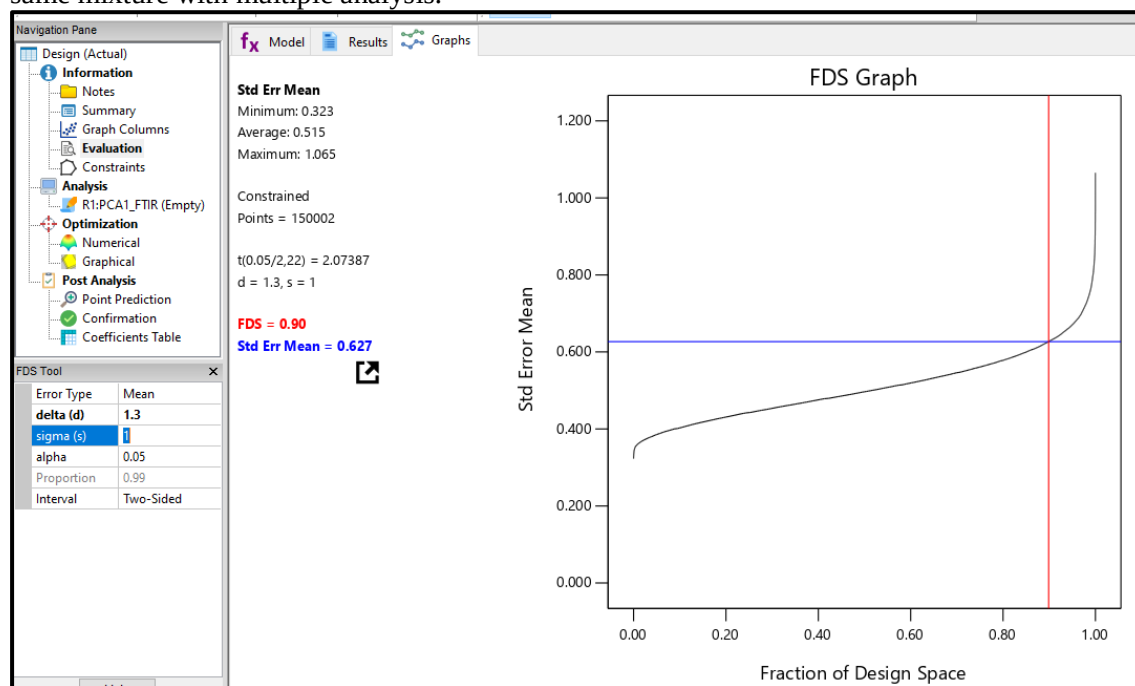


Figure 4-10. FDS plot of a {7, 2} optimal mixture design for the evaluation of precision of the design space of 52 mixtures consisting of prevalent SRF synthetic polymers under specific defined Design-Expert parameters: *Best Exchange* algorithm, I-optimal criterion, 1.3 signal-to-noise ratio, “mean” error type and 0.05 significance level.

Table 4-8 presents the final design space providing a matrix with the number of mixtures versus their composition that represents potential proportions of seven prevalent components in commercially produced SRF samples. The designed matrix was used for model training representing the output

matrix. The response matrix for hold-out validation and testing was designed by randomly selecting design points from **Table 4-8** (more information is presented in **Section 4.3.7**).

Table 4-8. Design space of the {7, 2} optimal mixture design aiming to simulate the typical composition of SRF based on its prevalent components: 52 mixtures defined the number of design points and mixture compositions defined the position of the design points. This design space constitutes the output training matrix of the model for composition identification of SRF.

Synthetic mixture	Cellulose	Hemicellulose	Lignin	HDPE	PP	PET	PVC
1	0.43	0.11	0.11	0.17	0.12	0.03	0.030
2	0.21	0.03	0.14	0.32	0.24	0.06	0.004
3	0.48	0.13	0.18	0.08	0.06	0.04	0.030
4	0.63	0.10	0.16	0.05	0.05	0.01	0.004
5	0.43	0.05	0.25	0.13	0.11	0.03	0.004
6*	0.21	0.07	0.11	0.28	0.19	0.14	0.012
7*	0.21	0.07	0.11	0.28	0.19	0.14	0.012
8	0.21	0.11	0.11	0.26	0.21	0.10	0.004
9**	0.36	0.06	0.16	0.20	0.15	0.07	0.015
10	0.21	0.03	0.13	0.29	0.26	0.07	0.021
11	0.53	0.05	0.13	0.12	0.08	0.06	0.010
12***	0.36	0.06	0.16	0.20	0.15	0.07	0.015
13	0.42	0.13	0.11	0.16	0.10	0.08	0.004
14	0.65	0.07	0.16	0.04	0.03	0.02	0.017
15	0.35	0.11	0.27	0.11	0.08	0.05	0.030
16	0.41	0.04	0.20	0.16	0.10	0.08	0.004
17	0.28	0.11	0.20	0.18	0.16	0.04	0.030
18	0.29	0.04	0.22	0.24	0.13	0.05	0.021
19	0.26	0.07	0.06	0.29	0.26	0.06	0.004
20***	0.36	0.06	0.16	0.20	0.15	0.07	0.015
21	0.21	0.11	0.11	0.30	0.20	0.06	0.012
22	0.21	0.06	0.06	0.28	0.26	0.10	0.030
23	0.21	0.03	0.07	0.37	0.21	0.12	0.004
24	0.28	0.07	0.22	0.16	0.15	0.08	0.030
25	0.21	0.05	0.05	0.36	0.23	0.07	0.030
26**	0.36	0.06	0.16	0.20	0.15	0.07	0.015
27	0.28	0.04	0.14	0.24	0.17	0.10	0.023
28	0.28	0.07	0.22	0.16	0.15	0.08	0.030
29	0.54	0.11	0.25	0.03	0.03	0.01	0.027

Synthetic mixture	Cellulose	Hemicellulose	Lignin	HDPE	PP	PET	PVC
30	0.21	0.03	0.16	0.25	0.22	0.12	0.012
31	0.21	0.03	0.09	0.39	0.20	0.08	0.010
32	0.47	0.05	0.15	0.16	0.14	0.03	0.004
33	0.29	0.09	0.22	0.24	0.12	0.05	0.004
34	0.26	0.03	0.07	0.28	0.19	0.14	0.030
35***	0.36	0.06	0.16	0.20	0.15	0.07	0.015
36	0.39	0.04	0.12	0.26	0.14	0.05	0.004
37	0.35	0.09	0.09	0.18	0.17	0.09	0.021
38	0.45	0.11	0.34	0.04	0.03	0.02	0.015
39	0.21	0.03	0.06	0.33	0.24	0.11	0.018
40	0.28	0.11	0.11	0.22	0.20	0.04	0.030
41	0.21	0.09	0.16	0.25	0.23	0.07	0.004
42***	0.36	0.06	0.16	0.20	0.15	0.07	0.015
43	0.24	0.03	0.06	0.28	0.25	0.14	0.004
44	0.39	0.04	0.10	0.21	0.19	0.04	0.030
45	0.21	0.03	0.06	0.33	0.24	0.11	0.018
46	0.46	0.07	0.35	0.04	0.03	0.01	0.030
47	0.21	0.11	0.16	0.24	0.16	0.09	0.030
48	0.29	0.06	0.07	0.33	0.17	0.07	0.004
49	0.63	0.10	0.16	0.04	0.05	0.01	0.004
50	0.21	0.06	0.06	0.24	0.30	0.10	0.030
51	0.28	0.04	0.14	0.28	0.12	0.10	0.023
52	0.47	0.05	0.15	0.21	0.08	0.03	0.004
53	0.36	0.06	0.16	0.26	0.09	0.07	0.015

*First replicate: identical composition; **Second replicate: identical composition, *** Third, fourth and fifth replicates: identical composition

4.3.5 Pre-processing before model construction

Before modelling, model pre-processing techniques related to sample (e.g. sample preparation), data (e.g. normalization and spectrum smoothing), and analysis (e.g. precision of analytical measurements) were applied.

4.3.5.1 Sample preparation

Sample preparation processes were applied to the samples for the design of the output training (synthetic mixtures), validation (waste mixtures from genuine SRF components) and testing (commercially produced SRF samples) datasets.

In relation to the output training set, special attention was paid to the sample preparation of the synthetic mixtures produced according to **Table 4-8**. Test samples (mixtures) with low mass were prepared (ca. 5 g) so that to obtain test portions as representative as possible. The smaller the difference between the sample mass – herein, the test portions – and the mass of the lot – herein, of the test samples –, the lower the sampling uncertainty (**Eq. 2-3**). Sample masses less than 5 g would be more difficult and time-consuming to properly handle especially for components with low proportions in the synthetic mixtures, e.g. PVC was ranged from 0.3-3% of total sample mass (**Table 4-7**). The proportions of the components in the mixtures (**Table 4-8**) were converted into mg with two decimal digits.

Some of the components of synthetic mixtures were on powder form (cellulose, xylan, lignin and PCV), while others were on pellet form (HDPE, PP, and PET). The latter polymers were primarily shredded with the cutting mill and secondarily with the cryomill selecting P4 program (4 grinding cycles, 2min grinding time, 1min intermediate cooling and 30 Hz grinding frequency). The masses of these polymers in the synthetic mixtures were weighted using a semi microbalance (METTLER TOLEDO) with 0.01 mg readability. For accurate measurements all necessary precautions were taken: i) horizontal positioning of the balance in an appropriate laboratory environment including controlled humidity, room temperature and a distance away from sunlight and doors; ii) regular scale calibration performed by technicians to ensure an accurate reading; iii) weighing with necessary equipment such as face mask, gloves, spatula and weigh boats made of polypropylene; iv) appropriate handling of samples such as placing the samples in the centre of the balance, weighing dry samples in room temperature, cleaning after each operation, closing the balance door and allow the reading to stabilize.

To avoid cross-contamination during weighting, I: i) weighted the masses of the first polymer for all mixtures; ii) placed the masses in small plastic bags for each mixture, concurrently with weighing; iii)

thoroughly cleaned the table and the balance after each polymer; iv) weighted the proportions of the second polymer for all mixtures; v) placed the masses in the bags, concurrently with weighing; etc. To homogenize the prepared mixtures from weighing even more, cryogenic shredding was repeated selecting P1(1grinding cycles, 3min grinding time, AND 30 Hz grinding frequency). The less extended shredding program was selected since the mixtures were already in a powder form. The cryogenically shredding to achieve a well mixing and avoid any melting of plastic fragments during shredding.

In relation to the hold-out validation set, the samples were prepared under identical sample preparation scenario with this of the training samples. Fossil-based and biomass materials resembling the prevalent polymers were drawn from commercially produced SRF samples (more information in **Section 4.3.7**), shredded with the cutting mill and cryomill (P4 program), weighted in the micro-balance and shredded again with the cryomill (P1).

In relation to the testing dataset (more information in **Section 4.3.8**), commercially produced SRF samples were subjected to sub-sampling and sample preparation processes according to the sub-sampling protocol reported in **Section 4.2.2** for the obtainment of one test sub-sample from each SRF sample.

4.3.5.2 Experimental data pre-treatment

Analytical data were obtained from the analysis of samples. Before model construction, some steps of analytical data pre-processing including normalization and smoothing of FTIR spectrum were followed.

Data normalization: Many researchers applied the min-max normalization (**Eq. 4-13**) in their datasets before conducting random forest (Linusson, 2013; Rahman et al., 2017; Haider et al., 2015; Lee et al., 2007; Xiao and Segal, 2009), although normalization is not necessary for random forest regression (Dinç et al., 2014). For that reason, the prediction error of MRF regression for normalized data was checked. Normalization was applied in the averaged analytical results obtained from the

replicate measurements (n=3). Three normalized datasets obtained – TGA, DTG, and FTIR – which all of them were used in model training.

$$y = \frac{x - \min}{\max - \min} \quad \text{Eq. 4-13}$$

FTIR smoothing: In material identification research, smoothing methods are usually applied in FTIR spectra to remove insignificant information or noise and keep mainly important signals (Kokalj et al., 2011). Smoothing techniques calculate the average group of data points, known as smoothing window, providing a plot of the average transmittance (or absorbance) versus wavenumber (ORIEL, 2016). The higher the number of data points in the average group, the higher the amount of smoothing data (ORIEL, 2016). However, smoothing a large amount of data may lead to the loss of significant information and therefore attention should be paid. There is a wide variety of FTIR smoothing techniques that were described by Tasumi (2014) and their performance is discussed by Cai et al. (2017). The most popular are the Moving-average smoothing and the Savitzky-Golay smoothing. Moving-average replaces a group of neighboring values by their arithmetic mean, while the Savitzky-Golay replaces the value at a given point by calculating the value from fitting a least-squares polynomial to a group of neighbouring points (Kokalj et al., 2011). Moving-average controls the degree of smoothing by defining the number of points averaged, while Moving-average by defining the polynomial degree and the number of neighboring points (Kokalj et al., 2011).

FTIR spectra were smoothed by both techniques, Moving-average smoothing and the Savitzky-Golay. Specifically, smoothing techniques applied in the average spectrum of the replicate measurements was obtained for each sample. Smoothing was carried out by using the package ‘spftir’ in RStudio V1.2 software. The default values of the smoothing window were kept: number of neighboring points equals to 21 for both techniques; and polynomial order equals to 2 for Savitzky-Golay. The algorithm of this package can be found in Valenzuela and Rodriguez-Llamazares (2016). Three different FTIR datasets obtained – raw, smoothed by Moving-average, and smoothed by Savitzky-Golay – which all of them were used in model training.

4.3.5.3 *Evaluation of precision of analytical measurements*

The analytical precision of TGA, DTG, and FTIR in input training, validation and testing sets of modeling was calculated to gain insights into the degree of agreement between the replicate measurements ($n = 3$). Reliable analytical measurements would give increase the model validity (Fay and Patterson, 2018). Precision, usually used as a measure of reliability, can be expressed as the % relative standard deviation of replicate measurements or as the relative standard deviation when the samples are different (König et al., 2013; Robinson et al., 2016). König et al. (2013) reported a recommended acceptable limit value of precision in laboratory analysis 10%, although higher values can be considered depending on the application area (Ramsey and Thompson, 2007).

Herein, the precision of each analytical technique was calculated for every input dataset (training, validation, and verification) separately. The separate calculation for each dataset is attributed to the fact that they consisted of samples with different characteristics leading to potentially different degree of inherent heterogeneity and therefore analytical precision. Analytical results for model training derived from synthetic mixtures, for model validation from actual SRF components, and for model testing from commercially produced SRF samples.

As mentioned before (**Section 4.3.2**), TG-DTG and FTIR provided a large number of data points, each of them corresponded to a specific predictor. In that case, the overall precision of analysis for the variables analysed in a sample can be determined by calculating the pooled relative standard deviation as conducted in **Section 4.2.8.3** for the calculation of AE (**Eq. 4-5**)

In **Eq. 4-5**, k was equal to 4321 for TGA and DTG, while for FTIR k was equal to 3601. By that way, the analytical precision of TGA, DTG and FTIR for each sample was calculated. In order to calculate the weighted average analytical precision for each input dataset (training, validation, and testing), **Eq. 4-5** was used again with the difference that k was equal to the number of samples of each dataset. For example, k was equal to 53 for the input training dataset. More information on validation and testing sets are given below (**Section 4.3.7** and **4.3.8**). This precision was compared with the uncertainty for TG-DTG of SRF (**Section 4.2.8.3**).

4.3.6 Model training

The supervised ML learning algorithm, MRF regression, was selected to generate a multivariate model that considers the relationship between output responses (polymers) using the defined mixture design space (**Table 4-8**) as output training set and analytical results as input training set. This multivariate model would constitute the tool for the composition identification of SRF based on its prevalent polymers.

In model training, with the use of RStudio packages, ensemble approaches with various combinations of inputs are examined so that to improve the model performance and therefore build a model with the minimum prediction error (Rahman, 2017). **Figure 4-11** illustrates a step by step overview of model training followed to address the research objective (**O4**). Specifically, a considerable number of datasets combinations derived from TGA, DTG, and FTIR datasets was obtained. The selection of the best combination was conducted with the use of evaluation metrics commonly used in regression (Hamner et al., 2018) following two different approaches: i) under constant tuning parameters (*mtry*, *Ntree*, and *Min_Leaf*); and ii) under variable *mtry* depending on the number of predictors. To ascertain the selection of the best combination in terms of model bias and variance (more details in **Section 4.3.6**), k-fold cross-validation applied in a number of combinations that had better performance than others based on the previous step. K-fold cross-validation was carried out for the combinations with the best model performance. At the final step of model training, hyperparameter tuning, the process of choosing a set of optimal tuning parameters for a ML algorithm (Schratz et al., 2019), through k-fold validation was applied in the best dataset combinations.

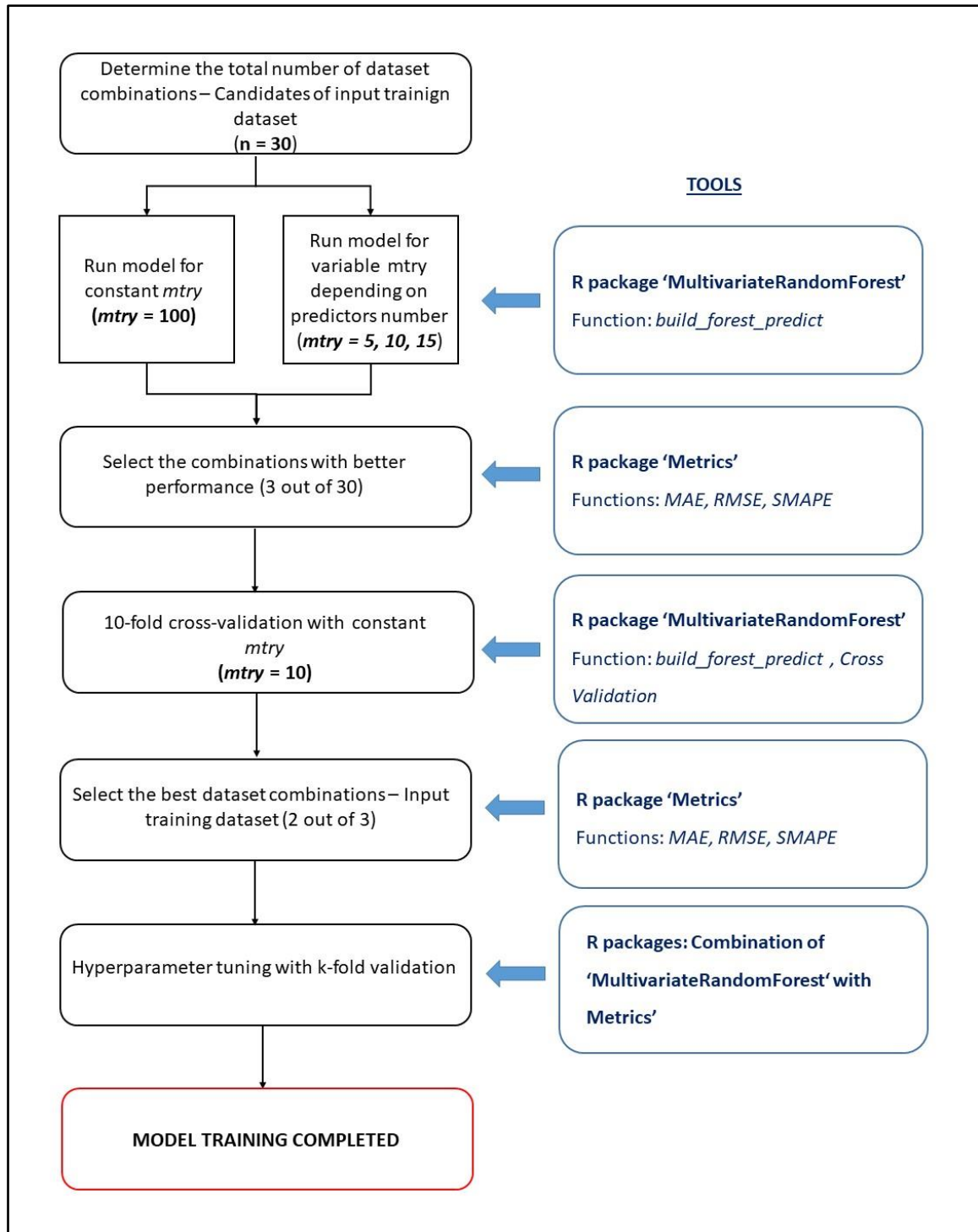


Figure 4-11. Overview of training of MRF regression model for the composition identification of SRF based on its prevalent components including ensemble approaches with various dataset combinations and a set of ML tools (R packages and related functions).

4.3.6.1 Packages and functions of ML algorithm

Package for MRF regression: The algorithm of MRF regression analysis for model construction was built using the R package ‘MultivariateRandomForest’ (Rahman, 2017) in RStudio V1.2 software.

Specifically, the function *build_forest_predict* was implemented to build the model of MRF regression with the use of the training dataset generating the prediction of training samples. To run this function, the following parameters had to be introduced:

- **trainX**: Input feature matrix of $M \times N$, M is the number of training samples (number of mixtures) and N is the number of input variables, which was defined by several dataset combinations obtained from analysis;
- **trainY**: Output response matrix of $M \times N$, M is the number of training samples and N is the number of output variables which was defined by the mixture design matrix (**Table 4-8**);
- **n_tree**: Number of trees in the forest, which must be positive integer (default value 500);
- **m_feature**, known as *mtry* parameter: The number of randomly selected input variables considered for each split in each regression tree node ($mtry < \text{number of predictors } (p)$);
- **min_leaf**: Minimum number of samples in the leaf node. If a node has less than or equal to **min_leaf** samples, then there will be no splitting in that node and this node will be considered as a leaf node ($Min\_Leaf \leq \text{number of samples } (N)$);
- **TestX**: Testing samples of size $Q \times N$, where Q is the number of testing samples and N is the number of features (same number of features as training samples).

The selected values of these parameters and related criteria for their selection are provided in the following Section (4.3.6.2).

Noted that, random forest can also be used for dimensionality reduction, known as variable importance technique, using the function *variable_importance_measure*. Variable importance indicates the number of times a predictor has been picked in the branch nodes of a (single) regression tree (Rahman, 2017). Variable importance can be used to rank the predictors in terms of their relative significance and therefore reduce the number of predictors. The implementation of this dimensionality reduction technique did not applied here. A dimensionality reduction in such wide data would induce pattern recognition and classification problems due to the drastic reduction usually sought in datasets with thousands of predictors. Additionally, variable importance techniques is a feature selection technique that might fail in correlated data, while the use of PCA might be preferred instead

(Wickramasinghe and Geisler, 2008). However, variable importance was successfully applied in spectroscopic data by Lee et al. (2013), who reported that random forest can be used in highly complex data.

Package for evaluation metrics:

These predicted values were evaluated through the scatter plots of observed versus predicted values along with coefficient of determination (R^2), and a variety of evaluation metrics calculated with the use of R package ‘Metrics’ provided by Hamner et al. (2018). Despite the need for robust model evaluation metrics, the choice of the most appropriate measure is still controversial (Hyndman, 2006; Davydenko and Fildes, 2016). There is a wide variety of metrics for regression, time series, classification, and information retrieval problems (Hamner et al., 2018), which can be grouped into two main categories (Hyndman, 2006; Botchkarev, 2018): i) scale-dependent measures including absolute and squared errors; and scale-free errors including percentage and relative errors. Scaled-dependent errors are mainly used to compare forecasting methods on the same set of data since their scale depends on the scale of data (Chen et al., 2017), while scale-free errors are used to compare performance across different datasets since they are scale independent (Hyndman, 2006).

Table 4-9 presents a short description of the most common metrics used to evaluate ML models including mathematical formulas, R functions and their limitations. Every evaluation metric has its disadvantages and therefore the selection of a single metric might lead to misinterpretation of the results (Davydenko and Fildes, 2016). Even with the selection of a suitable metric, a gap of information would always exist (Sentz and Hemez, 2013).

In random forest related studies, the use of mean squared error (MSE) was the most prevalent option (Miller et al., 2014; Quan and Valdez, 2018; Xiao and Segal, 2009; González et al., 2016). MSE is a traditional measure in regression, despite interpretation issues (squared error) and its sensitivity to outliers (high weight to large residuals) (Wallström, 2009). In random forest research, only one study used the root mean squared error (RMSE) to obtain interpretable results (Linusson, 2013). Second in order was the mean absolute error (MAE) which is interpretable (Rahman et al., 2017; Quan and

Valdez, 2018; Haider et al., 2015), but it does not solve the problem of scale dependence and sensitivity to outliers (Hyndman, 2006).

Another common metric in regression models is R^2 . It is considered that conventional regressors have excellent performance for low MAE and MSE and high R^2 score (Kailkhura et al., 2019). However, the selection of R^2 as an evaluation metric is not recommended, especially in wide matrices, due to its trend to be increased when the number of predictors is grown (Pardoe, 2012). R^2 as a metric to assess the model accuracy might lead to misinformed conclusions and therefore its role should be restricted as a goodness-of-fit measure for regression models (Li, 2017).

In multivariate analysis, a scale-free metric able to compare model performance between different responses is useful. However, studies that made use of relative (Haider et al., 2015; De'Ath, 2002) and percentage (González et al., 2016) errors were limited. The main problem with these types of errors is the influence of a denominator with low value resulting in error inflation (Wallström, 2009). As an alternative solution to these errors, symmetric mean absolute percentage error (SMAPE) was suggested as percentage error that can handle observations close to one (Makridakis, 1993). Although Goodwin and Lawton (1999) criticised SMAPE for its symmetric properties when applied in single observations, it has been considered as a better alternative to MAPE and relative errors (Makridakis and Hibon, 2000; Wallström, 2009; Tofallis, 2015) leading to select it for ML model evaluation. Herein, RMSE and MAE were selected to compare different dataset combinations for each component (polymer) as they were on the same scale, while root relative squared error (RRSE) and SMAPE were selected to make comparisons among the components for specific datasets.

Table 4-9. Common evaluation metrics to assess the ML model performance during training, validation and testing including related mathematical formulas, R functions, description and limitations.

Error	Type	Mathematical formula ¹	R function ²	Description	Limitation	Ref.
Mean absolute error	Scale-dependent	$MAE = \frac{1}{n} \sum_{i=1}^n [e_i]$	<i>mae</i>	Average absolute difference between the	Highly sensitive to outliers (skewed	(Chen et al., 2017;

Error	Type	Mathematical formula ¹	R function ²	Description	Limitation	Ref.
				observed and predicted values	distribution to the right)	Davydenko and Fildes, 2016)
Mean absolute percentage error	Scale-free	$MAPE = \frac{1}{n} \sum_{i=1}^n \left \frac{e_i}{y_i} \right * 100$	<i>mape</i>	Average absolute percent difference between the observed and predicted values	Asymmetric: penalises over-forecasting more than under-forecasting Infinite or undefined when y_i is zero	(Chen et al., 2017)
Median absolute error	Scale-dependent	$MdAE = MEDIAN[e_i]$	<i>mdae</i>	Median absolute difference between the observed and predicted values	Not easily amendable, might contain bias	(Manikandan, 2011)
Mean squared error	Scale-dependent	$MSE = \frac{1}{n} \sum_{i=1}^n e_i^2$	<i>mse</i>	Average squared difference between the observed and predicted values	More sensitive to outliers than MAE Interpretation results due to different scale than original data	(Chen et al., 2017)
Root mean squared error	Scale-dependent	$RMSE = \sqrt{MSE}$	<i>rmse</i>	Root mean squared difference between the observed and predicted values	Also sensitive to outliers, but preferable than MSE	(Chen et al., 2017)
Root relative squared error	Scale-free	$RRSE = \sqrt{\frac{\sum_{i=1}^n e_i^2}{\sum_{i=1}^n (\bar{y} - y_i)^2}}$	<i>rrse</i>	Provides the squared error of the predictions relative to a naive model that	A normalized form of RMSE	(Hyndman, 2006)

Error	Type	Mathematical formula ¹	R function ²	Description	Limitation	Ref.
				predicted the mean for every data point		
Symmetric mean absolute percentage error (smape)	Scale-free	$SMAPE = \frac{1}{n} \sum_{i=1}^n \frac{ e_i }{(y_i + \hat{y}_i)},$ * 100	<i>smape</i>	Symmetric mean absolute difference between the observed and predicted values	Its symmetric property has been criticized	(Chen et al., 2017; Goodwin and Lawton, 1999)

¹ e_i is equal to predicted ($\hat{y}_i$) minus the observed (y_i) value; ²(Hamner et al., 2018)

K-fold cross-validation: In the stage of k-fold cross-validation for the selection of the best dataset combination, the *Cross Validation* function applied generating a number of cross-validation input and output matrices from training dataset depending on the defined k-fold (Rahman, 2017). K-fold cross-validation is a validation technique incorporated into model training that is widely used for hyperparameter tuning in ML (Rahman et al., 2017; Janitza and Hornung, 2018). In k-fold cross-validation, the training dataset is randomly split into k distinct folds of approximately equal sizes, from which k-1 folds are used for model training and the remaining fold is used for model testing (Rahman et al., 2017). This process is repeated k times selecting a different fold to hold out for testing (Rahman et al., 2017). The cross-validation accuracy is computed as the average accuracy over the k testing folds (Rahman et al., 2017; Janitza and Hornung, 2018). Noted that k-fold cross-validation error is determined from k models that are fit based on only a subset of the data (k-1 folds) yielded to a slight overestimation of real model prediction error that would be obtained for a model that fits the whole dataset (k folds) (Janitza and Hornung, 2018).

K-fold cross-validation is the most popular method to address overfitting issues without the generation of a new separate validation set is k-fold cross-validation. Herein, the risk of overfitting needs examination due to the high width of dataset combinations. For example, a dataset combination

of TGA (4,321 points) with DTG (4,321 points) and FTIR (3,601 points) equals to 12,243 input variables, while the single FTIR dataset equals to 3601 input variables.

Although k is still an unfixed parameter, most researchers selected as k number in cross-validation the value of 10 (Quan and Valdez, 2018; Janitza and Hornung, 2018; Haider et al., 2015; Liaw and Wiener, 2002; Linusson, 2013) or 5 (Haider et al., 2015; Wan and Pal, 2013; Rahman et al., 2017). It was selected 10-fold cross-validation and the predictions from all set aside testing sets were obtained assessing the performance once. Specifically, the predicted values of set aside datasets were obtained by running the function *build_forest_predict* 10 times and then re-running the function *build_forest_predict* using as input matrix the input training dataset ($M = 53$) and as testing matrix the predicted values from 10-fold cross-validation ($M=53$). Herein, 10-fold cross-validation was used for the selection of the optimal *mtry*, *Ntree*, and *Min_Leaf* in terms of model prediction.

4.3.6.2 Selection of best dataset combinations with two approaches

For D different datasets, $2^D - 1$ input dataset combinations will be provided (Rahman et al., 2017).

Herein, three analytical datasets ($D = 3$) from TGA, DTG and FTIR analysis were obtained leading to seven input dataset combinations, called *raw* datasets. Despite them, the normalized datasets were also obtained (**Section 4.3.5.2**) to check whether model performance would be better leading to seven more combinations. Additionally, two smoothing techniques in FTIR spectra were applied (Moving-average and Savitzky-Golay) resulting in four extra combinations from each smoothing technique for both raw and normalized datasets. After that, the total number of dataset combinations was equal to 30 consisting of 7 raw dataset combinations, 7 normalised, 8 smoothed and 8 smoothed and normalised (**Table 4-10**).

Table 4-10. Input dataset combinations derived from TGA, DTG, and FTIR analytical techniques that were run in ML algorithm (MRF regression) to obtain the combination with the best performance in terms of model accuracy for the prediction of SRF composition based on its prevalent components.

Dataset	Name	No. input variables /No. datasets	Data pre-treatment technique
1 st	Raw DTG	4,321 / 1	As received from analysis
2 nd	Raw TGA	4,321 / 1	

Dataset	Name	No. input variables /No. datasets	Data pre-treatment technique
3 rd	Raw FTIR	3,601 / 1	
4 th	Raw TG-DTG	8,642 / 2	
5 th	Raw TG-FTIR	7,922 / 2	
6 th	Raw DTG-FTIR	7,922 / 2	
7 th	Raw TG-DTG-FTIR	12,243 / 3	
8 th	Normalised DTG	4,321 / 1	Normalisation
9 th	Normalised TGA	4,321 / 1	
10 th	Normalised FTIR	3,601 / 1	
11 th	Normalised TG-DTG	8,642 / 2	
12 th	Normalised TG-FTIR	7,922 / 2	
13 th	Normalised DTG-FTIR	7,922 / 2	
14 th	Normalised TG-DTG-FTIR	12,243 / 3	
15 th	FTIR_MA	3,601 / 1	Smoothing (MA: Moving-average – SG: Savitzky-Golay)
16 th	FTIR_SG	3,601 / 1	
17 th	TGA-FTIR_MA	7,922 / 2	
18 th	TGA-FTIR_SG	7,922 / 2	
19 th	DTG-FTIR_MA	7,922 / 2	
20 th	DTG-FTIR_SG	7,922 / 2	
21 st	TGA-DTG-FTIR_MA	12,243 / 3	
22 nd	TGA-DTG-FTIR_SG	12,243 / 3	
23 rd	Normalised FTIR_MA	3,601 / 1	Smoothing (MA: Moving-average – SG: Savitzky-Golay) & Normalisation
24 th	Normalised FTIR_SG	3,601 / 1	
25 th	Normalised TGA_FTIR_MA	7,922 / 2	
26 th	Normalised TGA_FTIR_SG	7,922 / 2	
27 th	Normalised DTG_FTIR_MA	7,922 / 2	
28 th	Normalised DTG_FTIR_SG	7,922 / 2	
29 th	Normalised TGA_DTG_FTIR_MA	12,243 / 3	
30 th	Normalised TGA_DTG_FTIR_SG	12,243 / 3	

The reason that I followed two different approaches (variable *mtry* and constant *mtry*) to select the best dataset combination was that *mtry* is a parameter dependent on the number of predictors.

Specifically, the traditional default value of *mtry* is equal to 1/3 of the number of predictors (Zhang et al., 2019; Tyrallis et al., 2019; González et al., 2016; Liaw and Wiener, 2002). However, when the number of input variables is considerably large and the correlation among them is high, small values of *mtry* can notably improve the model accuracy (Tyrallis et al., 2019; Segal and Xiao, 2011). Since the process of *mtry* optimisation is far more than conclusive (Tyrallis et al., 2019), it was decided to train the model following these two approaches obtaining higher confidence about the validity of the results. Firstly, a low constant value 10 in the *mtry* parameter was defined for all combinations. In second approach, the values of *mtry* were increased proportionally to the number of predictors of each dataset combinations. So, in the second approach, it was decided to set the *mtry* to: i) 5 for single datasets (1st, 2nd, 3rd, 8th, 9th, 10th, 15th, 16, 23rd, and 24th); 10 for combinations with two datasets, in which the number of predictors was almost twice higher compared to single datasets (4th, 5th, 6th, 11th, 12th, 13th, 17th, 18th, 19th, 20th, 25th, 26th, 27th, and 28th); and iii) 15 for combinations with three datasets (21st, 22nd, 29th, and 30th), in which the number of predictors was almost three times higher compared to single datasets. In the next stage of k-fold cross-validation before hyperparameter tuning for the selection of final best combinations, *mtry* was defined 10.

In the entire process of model training for the selection of best dataset combinations including the two approaches and k-fold cross-validation, *Min_Leaf* was set at 3, while *Ntree* was increased in the step of cross-validation. In the first step of model training with the two different approaches, *Ntree* was kept at the default value of 500, while in the stage of k-fold cross-validation *Ntree* was increased at 1000 since the number of datasets was lower compared to the previous step (only 3 out of 30) enabling to increase the computation time and potentially obtain better performance.

4.3.6.3 Hyperparameter tuning

In random forest, the human intervention is restricted to define the number of trees of the forest (*Ntree*), the number of variables randomly chosen to be considered for each split in the individual trees (*mtry*) and the depth of every individual tree (*Min_Leaf*) (González et al., 2016). The default values given by the related R package for parameters *mtry*, *Ntree* and *Min_Leaf* is equal to 1/3 of the

number of predictors, 500 and 5, respectively (Tyralis et al., 2019). However, the major handicap of these default values, is the absence of theoretical and empirical justification (Scornet, 2017). The optimal values of these parameters might be considerably different from the defaults values and therefore their choice is case study-dependent (González et al., 2016). Rahman et al. (2017) reported a range of suggested values for tuning parameters that is presented in **Table 4-11**. In principle, hyperparameter tuning is conducted through cross-validation (Janitza and Hornung, 2018; Segal and Xiao, 2011; Zhang et al., 2019).

In general, small values are recommended for the parameter *Min_Leaf* that is used to stop the tree expansion affecting the size of the tree (Tyralis et al., 2019). However, *Min_Leaf* has less influence on the performance of algorithm compared to *Ntree* and *mtry* (Tyralis et al., 2019).

Ntree has a direct influence in prediction accuracy relying on the fact that the higher the number of trees, the smaller the prediction error (González et al., 2016). However, this relationship is asymptotic since further increase for large *Ntree* would not lead to significant improvements (González et al., 2016). Besides, increasing the number of trees leads to the linearly increase of computational time (Rahman et al., 2017) and therefore a trade-off solution between the predictive performance and computational time should be found (González et al., 2016; Tyralis et al., 2019; Janitza and Hornung, 2018). It is recommended to increase the number of trees until a stabilization of the results is reached (Boulesteix et al., 2012). When the number of predictors is large, *Ntree* can be set as large as computational time is feasible (Janitza and Hornung, 2018; Tyralis et al., 2019).

The value of *mtry* defines the size of a subset of input variables that is randomly selected from all candidate predictors at each split. The scope for the selection of a random subset instead of all predictors is to reduce the correlation between trees and therefore obtain dissimilar trees resulting in the reduction of variance (Janitza and Hornung, 2018). Breiman (2001) reported that random forest enjoy exceptional accuracy that is attained for a wide range of settings of *mtry*. Despite the default value, the main criterion for the selection of optimal *mtry* was to consider the correlation amongst predictors (González et al., 2016). It is recommended, the higher the correlation, the lower the *mtry*

values (Gareth et al., 2013). However, too small *mtry* may lead to the selection of irrelevant variables for a split leading to inaccurate trees. In contrast, if *mtry* is too large, the correlation among trees is increased leading to higher variance (Quan and Valdez, 2018). Similarly to *Ntree*, the computation time should also be considered for the selection of *mtry* (Rahman et al., 2017; Tyralis et al., 2019). Herein, hyperparameter tuning was conducted through 10-fold cross-validation in a wide range of MRF parameters, which is presented in **Table 4-11**. The parameters did not exceed the value of 500 for *mtry* and 2,000 for *Ntree* due to high computation time. For example, the computation time by selecting these maximum values (*mtry* = 500 and *Ntree* = 1,000) was more than 5 hours at each fold for such a wide input dataset consisting of thousands of variables. Thus, the predicted values for this set of tuning parameters were obtained by running 10 models (10-fold cross-validation) for 5 hours each.

Table 4-11. Feasible and suggested ranges of tuning parameters for MRF regression along with the selected values for hyperparameter tuning of this research. Adapted by Rahman et al. (2017).

Tuning parameter	Feasible range	Suggested ranges	Selected values of this research
<i>mtry</i>	[1, sample size]	1-10	5, 10, 15, 20, 30, 40, 50, 100, 500
<i>Ntree</i>	[1, ∞]	100-500	250, 500, 600, 800, 1,000, 1,500, 2,000
<i>Min_Leaf</i>	[1, number of predictors]	5-50	3, 4, 5, 10

4.3.7 Model validation

There are several techniques to validate a ML model which are grouped into two main categories: i) cross-validation where the same dataset is used for training and validation, with the most common being k-fold (Arlot and Celisse, 2010), and ii) forward-validation where a subset of the available data is selected for training and a separate subset for validation, with hold-out validation being the simplest forward validation scheme (Schnaubelt, 2019). In hold-out validation, available data is split into two different subsets under different proportions (most common ratios: 70/30, 50/50, or 75/25 (Pang and Jung, 2013; Bayley and Falessi, 2018)) for training and validation, respectively.

Cross-validation techniques tend to provide a pessimistically biased estimate (Janitza and Hornung, 2018), but they use the available data more efficiently in the sense that every observation contributes to model validation (Schnaubelt, 2019). On the other hand, forward-validation schemes provide an unbiased estimation, but the model is trained with less observations resulting in issues of high variance (Schnaubelt, 2019). A recent research compared eight popular validation techniques in ML including both types for non-stationary time series data (Schnaubelt, 2019). Results showed that the selection of the appropriate validation scheme depends on dataset size, ML algorithm and type of dynamics (time-dependence of observations) (Schnaubelt, 2019). Yet, forward-validation outperformed the cross-validated schemes with respect to both bias and variance (Schnaubelt, 2019).

Herein, despite cross-validation with synthetic mixtures (training dataset), the MRF model was validated with a hold-out dataset able to offer insights into model applicability in genuine SRF samples. The model was trained and cross-validated with synthetic mixtures, but considerable differences might be observed regarding the thermal behaviour of synthetic and genuine SRF samples (Grammelis et al., 2009; Cuperus et al., 2005) due to cross-contamination, presence of impurities and/or other unidentified substances (Silva et al., 2015; Mumbach et al., 2019).

For that reason, a hold-out set from genuine SRF components was prepared. Six waste mixtures ($n = 6$) accounted for ca. 10% of training set ($n=53$) consisted of fossil-based waste items that represented PE, PP, PET and PVC, and wood and paper that represented cellulose, hemicellulose and lignin. Specifically, single plastic, paper and wood items were obtained through manual sorting from commercially produced SRF samples, which were subjected to FTIR for polymer identification. It is extremely hard if not impossible to obtain pure polymers from genuine waste samples. Thus, waste selected items that had an FTIR spectrum considerably matching to the counterpart polymers were considered representatives of these polymers. In case of plastics, the polymer identification process was quite straightforward, but not for wood and paper that were selected to represent the biopolymers. The proportions of biomass prevalent components (cellulose, hemicellulose, and lignin) into the waste items of paper and wood were quantified considering the critical review analysis (**Section 4.1.2.1**), as occurred to define the design space (**Section 4.3.4**).

After identification of prevalent SRF polymers in waste items extracted from SRF sample, mixtures were prepared (**Section 4.3.5.1**) under different proportions defined considering the design space (**Table 4-8**). Specifically, the design points 1, 4, 15, 21, 52, and 53 were randomly selected from **Table 4-8** to prepare the hold-out validation mixtures (**Table 4-12**). I considered to select design points in which the biomass and plastic fraction would be widely variable to cover as more of the design space as possible (e.g. biomass fraction ranged between 42 and 89% w/w in the mixtures).

Noted that the composition of the validation mixtures was not identical with this of the corresponding design points due to experimental interventions in the stage of weighting so that to obtain rounded values for mixture masses. In addition, proportions of cellulose, hemicellulose and lignin in validation mixtures were considerably different from those in the selected design points since critical review analysis on the weight percentage of biopolymers in biomass fractions such as wood and paper was fully completed after the sample preparation of validation mixtures. Moreover, the proportion of PVC was kept at low levels into the validation mixtures (between 0.31-0.41% w/w) independently to the proportions of PVC in the selected design points to ascertain that Total [Cl] in the hold-out validation mixtures is not high. Keeping low levels of Total [Cl] in the samples was a requirement of laboratory technicians as high Cl levels might cause corrosion in the furnace (Operation Instruction, 2012).

However, these practicalities did not hamper to obtain a validation set in which the proportions of components lied within the specified ranges of the design space (**Table 4-7**). In other words, all complex constraints were met in the hold-out validation set with the only exception being the proportion of hemicellulose in the second sample that derived from the design point 4 which is equal to 17.6% w/w (**Table 4-12**), while the upper bound of hemicellulose was set at 13.3% (**Table 4-7**). However, this exception would offer insights into the ability of MRF algorithm to make predictions outside the range of response values. The proportions of prevalent SRF polymers in hold-out validation mixtures is presented in **Table 4-12**. Despite the uncertainty contained in the quantification of proportions of biopolymers since an accurate quantification is obtained only with analytical determination, the weight percentage of biomass fraction (summation of cellulose, hemicellulose and lignin) derived from wood and paper, of plastic fraction, and its components (PE, PP, PET, and PVC)

was accurately quantified enabling to reliably estimate the model performance. Analytical results (TGA, DTG, and FTIR) represented the input validation matrix, whereas the composition of six waste mixtures consisting of genuine SRF components represented the output validation matrix.

Table 4-12. Proportions (% w/w) of mixtures consisting of biomass (paper and wood) and fossil-based (plastics) waste items extracted through manual sorting from commercially SRF sample with respect to prevalent SRF polymers (cellulose, hemicellulose, lignin, PE, PP, PET, and PPVC) that indicated the response matrix of the hold-out validation set with a goal to evaluate the model performance in genuine SRF samples considering the presence of cross-contamination, impurities and unidentified materials.

Waste mixture	Design points ¹	Biomass					Plastics			
		Paper ²	Wood ³	Cellulose	Hemicellulose	Lignin	PE	PP	PET	PVC
1	1	0.36	0.29	0.39	0.13	0.12	0.18	0.13	0.04	0.004
2	4	0.53	0.36	0.55	0.18	0.16	0.05	0.05	0.01	0.003
3	15	0.51	0.22	0.47	0.13	0.12	0.12	0.09	0.06	0.004
4	21	0.32	0.11	0.28	0.08	0.07	0.31	0.20	0.06	0.003
5	52	0.57	0.10	0.46	0.11	0.10	0.21	0.09	0.03	0.003
6	53	0.58	0.00	0.42	0.09	0.07	0.26	0.09	0.07	0.003

¹ The composition of waste mixtures (proportions of polymers) used as the response matrix of hold-out validation set was determined based on the corresponding design points presented in **Table 4-8**; ² Assuming that cellulose, hemicellulose and lignin in paper items is 72.6, 14.9, and 12.5% w/w, normalised values received from critical review analysis (**Section 5.2**); ³ Assuming that cellulose, hemicellulose and lignin in wood items is 47, 27.2, and 25.8% w/w, normalised values received from critical review analysis (**Section 5.2**)

Noted that the issue of higher variance in model performance with the hold-out validation is not applicable here, since hold-out validation set was not supposed to be a part of available data in model training: the validation mixtures from genuine waste components had different composition from synthetic mixtures. The reason for this difference was to evaluate the model performance in real samples when cross-contamination, impurities and unidentified materials is present.

4.3.8 Model testing

Model testing is carried out only once the model construction has been completed (trained and validated) to obtain an independent and unbiased evaluation of model performance when used in ‘real world’. The test dataset is a hold-out set that is used as a single evaluation rather than as a determinant of model accuracy. Herein, the test dataset derived from the analysis of commercially

produced SRF samples obtained from MT/MBT plants to evaluate the model performance in genuine SRF. Specifically, the composition of four SRF samples was specified through manual sorting into specific waste component categories including: *paper/cardboard*, *wood*, *plastic films*, *soft plastics*, *hard plastics*, *textiles*, *foam*, and *finer* (cumulative passing < 15mm) following the guideline of CEN/TC 343 standard for determination of SRF biogenic content (BS EN 15440, 2011), as presented in **Table 4-13**.

Table 4-13. Composition of commercially produced SRF samples obtained from two different MT/MBT plants in the UK determined through manual sorting into specific waste component categories.

SRF sample ¹	Sample mass (kg)	Paper/ cardboard (% w/w)	Plastic film (% w/w)	Soft plastic (% w/w)	Hard plastic (% w/w)	Wood (% w/w)	Textiles (% w/w)	Foam (% w/w)	Fines ² (% w/w)
1-1	0.82	29.4	8.1	7.9	8.9	12.4	9.3	2.1	21.9
1-2	0.86	28.7	8.9	7.6	7.2	11.7	12.4	1.0	22.4
2-1	0.84	43.1	7.2	15.1	3.7	5.7	6.2	1.8	17.2
2-1	0.88	44.1	7.3	8.6	5.6	6.1	7.1	3.3	17.9

¹ Samples derived from two different MT/MBT plants in the UK (1-1 and 1-2 samples from the one plant and 2-1 and 2-2 from the other plant); ² cumulative passing < 15mm

However, the samples of testing dataset were more heterogeneous than these of the hold-out validation due to the presence of a wider and more complex (e.g. presence of fines) variety of waste items and materials. Thus, the consideration of typical content of polymers in main waste item categories obtained from critical review analysis (**Section 5.2**) to consider the composition of SRF samples would not be an accurate approach. In addition, the accurate experimental determination of the proportions of prevalent polymers into these samples was not feasible with the existing available resources and equipment in a timely manner.

Scatter plots of observed versus predicted values were obtained only for the biomass and plastic fraction. The predicted values of biomass content were considered as the summation of cellulose, hemicellulose, and lignin and of plastic fraction as the summation of PE, PP, PET, and PVC, as received from model prediction. In order to calculate the biomass and plastic content of the observed

values, some assumptions were followed: i) the textile fraction was composed of 9% w/w natural fibers and 91% w/w synthetic fibers, these values were obtained by an industrial database that reported the global production of synthetic and cellulosic fibers in 2018 (Statistica, 2018); ii) the biomass and plastic fraction in unidentified materials ('foam' and 'fines') was similar to the composition of the identified sample mass. By taking into account these assumptions, the composition of samples from **Table 4-13** was normalized into biomass (*paper/cardboard, wood and natural fibers*) and plastic fraction (*plastic films, soft plastics, hard plastics, and synthetic textiles*) leaving out the unidentified materials (*foam and fines*). In addition to this, the content of biomass and plastic fraction in SRF samples was determined by calculating the weight loss induced in a temperature range from the onset to endset temperature of each DTG peak, respectively (Robinson et al., 2016). By that, ML model efficiency performance was compared with TG-DTG and manual sorting.

4.3.9 Summary of experimentation for DoE2

The main steps of DoE2 to develop a ML model for composition identification of SRF at polymer level were: i) training with 53 synthetic samples; ii) 10-fold cross-validation with 53 synthetic samples; iii) hold-out validation with 6 waste mixtures; and iv) model testing with 4 commercially produced SRF samples. These steps were executed by analyzing a number of test samples with different characteristics presented in **Table 4-14**.

Table 4-14. Total number of test samples and measurements taken with the use of TG-DTG and FTIR for DoE2 so that to develop a ML model for composition identification of SRF at polymer level.

Model steps	No. test samples	No. measurements ¹	Type of sample	Reference Table ²
Training Cross-validation*	53	159	Synthetic	Table 4-8
Hold-out	6	18	Waste mixtures	Table 4-12
Testing	4	12	Commercially produced SRF samples	Table 4-13
Total	63	189		

¹ Three replicate measurements for each test sample; ² Table that provides more information for the corresponding dataset; * Model training and cross-validation were conducted by using the training dataset

5 RESULTS

This chapter provides a series of results that are presented in the order they appear in the chapter of methodology (**Chapter 4**), as far as possible, pertaining to the objectives of this research.

5.1 Variability of Cl and its fate when SRF co-combusted in cement kilns

At this section the results of systematic critical review analysis following the PRISMA methodology (**Section 4.1.1**) to assess: the variability of Cl in SRF samples and therefore identify the challenges at the stage of pre-processing (**Section 5.1.1**); and obtain a better understanding of its fate during SRF co-combustion in cement kilns therefore identify the challenges at the stage of co-processing (**Section 5.1.2**), addressing the research objective (**O1**).

5.1.1 Quantification of Cl variability in commercially produced SRF samples

Chlorine content in MSW

Typical values of Total [Cl] in MSW reported in previous studies are presented in **Table 5-1**. The 95% confidence interval of Cl content in MSW was $1.00 \pm 0.35\%$ w/w_d and the minimum and maximum values were 0.37% w/w_d and 1.94% w/w_d, respectively. This is in line with a report that summarized the best practices in the cement industry and reported that the Total [Cl] in MSW ranged between 0.5-1.5% w/w (Sharabaroff et al., 2017). Also, **Table 5-1** presents the proportion of organic and inorganic Cl present in MSW, which was in the range of 50-75% and 50-25% of the Total [Cl], respectively. Data on the combustible and incombustible Cl was limited.

Table 5-1. Dataset of typical values of Total [Cl] in MSW as received reporting basis.

Type	Total [Cl] (% w/w _d)	Inor. [Cl] (% of Total Cl) ¹	Or. [Cl] (% of Total Cl) ²	Com. [Cl] (% of Total Cl) ³	Incom. [Cl] (% of Total Cl) ⁴	Analytical method	No. samples ⁵	Ref.
MSW ^d	0.46 0.89	24.4 24.2	75.6 75.8			ASTM E775-81	15	(Domalski et al., 1986)
MSW	0.46	50.0	50.0	82.3	17.7	Quartz combustion	n.d. ^a	(Kanters et al., 1996)

Type	Total [Cl] (% w/w _d)	Inor. [Cl] (% of Total Cl) ¹	Or. [Cl] (% of Total Cl) ²	Com. [Cl] (% of Total Cl) ³	Incom. [Cl] (% of Total Cl) ⁴	Analytical method	No. samples ⁵	Ref.
MSW	0.37					Solid waste incineration system	13	(Chang et al., 1998)
MSW	1.05					BC-IC	n.d. ^a	(Sørum and Task, 2001)
MSW	0.59			75.4	24.6	Quartz furnace-IC	n.d. ^{a,b}	(Watanabe et al., 2004)
Household waste	0.85					ICP-SFMS	n.d. ^{a,b,c}	(Riber et al., 2009)
MSW ^e	1.27 1.63	33 21	67 79			Eschka method	4 3	(Prawisudha et al., 2012)
MSW	1.50					ISO 10304-1:2009	n.d. ^a	(Nasrullah et al., 2017)
MSW	1.94					EA	n.d. ^a	(Chen et al., 2015a)
Arithmetic mean	1.00 (0.65, 1.36)*							
CV (%)**	52.76							
d.f.***	10							

¹ Inorganic; ² Organic; ³ Combustible; ⁴ Incombustible; ⁵ Number of independent measurements; ^a n.d.: not determined; ^b Calculated based on MSW composition and Cl values of hand-sorted MSW fractions; ^c Batches of 80-1200 tonnes of household waste from 3 different cities collected for the calculation of Cl; ^d for two different cities, Baltimore County, Maryland and New York, Brooklyn; ^e two different MSW samples; * Lower and upper 95% confidence interval; ** Coefficient of Variation; *** Degrees of freedom

Chlorine content in SRF

Typical values of Total [Cl] in SRF are presented in **Table 5-2**. The 95% confidence interval was 0.76 ± 0.14% w/w_d; with minimum and maximum values of 0.31% w/w_d and 1.38% w/w_d, respectively. The results are in agreement with Gendebien et al. (2003), reporting that a typical Total [Cl] of WDF from household waste is in the range 0.3-1% w/w. A wider range was given by Cortada Mut et al. (2015) of 0.1 to 3.9% w/w_d. For a particular SRF, with a high PVC content, Total [Cl] was reported at > 1% w/w_d (Sarc et al., 2014).

Table 5-2. Dataset of typical values of Total [Cl] in SRF as received reporting basis.

Type	Total [Cl] (% w/w _a)	Analytical method	Origin (type of waste)	No. samples ¹	Ref.
SRF ²	0.31	Incineration system	MSW	15	(Chang et al., 1998)
SRF _{SBS} ³	0.57	Combustion -IC	MSW and commercial	n.d. ^a	(Hilber et al., 2007a)
SRF	0.71	BC-IC	MSW	45	(Velis, 2010)
SRF	0.41	Data from supplier	C&I	n.d. ^a	(Vainikka et al., 2011)
SRF	0.45	BC-IC	C&I	2	(Vainikka et al., 2011)
SRF	0.69	BC-IC	Household and commercial	30	(Velis et al., 2012)
SRF	0.85	BC-IC	Household and industrial	10	(Aldrian et al., 2016)
SRF _{SBS} ³	0.49 0.89	BC-IC	MSW	n.d. ^a	(Glorius, 2014)
SRF ⁴	1.38 1.08	BC-IC	Several streams	15 21	(Sarc et al., 2014)
SRF	0.71 0.80	ISO 10304- 1:2009	MSW, C&I	3 3	(Nasrullah et al., 2017)
SRF ⁵	0.91 0.69 1.19	BC-IC	MSW	3 9 6	(Edo-Alcón et al., 2016)
SRF	0.92	Eschka method	MSW	70	(Spurek, 2012)
SRF	0.60	BC-IC	MSW	3	(Nasrullah et al., 2016)
Arithmetic mean	0.76 (0.62, 0.90)*				
CV (%)**	36.70				
d.f.***	17				

¹Number of independent measurements; ²It is reported as refuse derived fuel (RDF) similar to SRF without compliance with EU specification, due to oldness of the study; ³SRF developed by the German organisation Remondis; ⁴Different qualities of SRF provided by different suppliers; ⁵MSW reject flows form 3 different MBT plants; ^a n.d.: not determined;

* Lower and upper 95% confidence interval; ** Coefficient of Variation; *** Degrees of freedom;

Chlorine content in waste component categories

Typical values of Total [Cl] in waste component categories of MSW and consequently SRF are shown in **Table 5-3**. *Rubber-leather* has the highest average Cl content, indicating its potential role on [Cl] load in SRF. However, the category *rubber-leather* covers a wide range of materials, and the limited number of observations give rise to inconsistent [Cl] values and prevent any further estimation.

Table 5-3. Dataset of typical values of Total [Cl] in waste component categories as received reporting basis.

	Plastics	Paper/ cardboard	Wood	Textiles	Rubber- leather	No. samples ¹	Ref.
Total [Cl] (% w/w _d)	1.14	0.15	0.05	1.10	8.00	3	(Nasrullah et al., 2016)
	1.84	0.50	0.10	0.40	2.20	3	(Rotter et al., 2004)
	0.54	0.27	0.40	0.32	0.36	n.d. ^a	(Guo et al., 2001)
	3.62	0.41	0.39	1.19	7.00	n.d. ^a	(Uchida et al., 1988)
	1.55	0.10	0.27	1.17	-	2	(Ma et al., 2010)
	2.40	0.18	0.23	0.41	-	4	(Watanabe et al., 2004)
	3.88	0.30	-	-	-	n.d. ^a	(Sørsum and Task, 2001)
	2.62	0.24	0.22	0.22 ^b 0.23 ^b	0.76	18 ¹ 2 ^{2,3,4,5}	(Chiemchaisri et al., 2010) ¹ , (Velis, 2010) ^{2,3,4,5}
		0.33 ^c 0.04 ^c	0.98			n.d. ^a	(Heikkinen et al., 2004)
		0.25 ^d 0.21 ^d				15	(Domalski et al., 1986)
Arithmetic mean	2.20 (1.23, 3.17)*	0.25 (0.17, 0.33)*	0.33 (0.09, 0.57)*	0.63 (0.26, 1.00)*	3.66 (0.36, 8.00) ^{II}		
CV (%)**	52.94	51.59	87.83	64.75	97.86		
d.f. ^{***}	7	11	7	7	4		

^{1,2,3,4,5} refer to *Plastics*, *Paper/cardboard*, *Wood*, *Textiles* and *Rubber-leather*, respectively; ^a n.d.: not determined; ^b each value corresponds to textiles/fabrics and carpets/mats, respectively; ^c each value corresponds to cardboard and glossy paper; ^d the values derived from two different cities; * Lower and upper limits of 95% confidence interval for sample mean; ** Coefficient of Variation; *** Degrees of freedom; ¹ Number of independent measurements * No. replicates per sample; ^{II} range between minimum and maximum used due to data inconsistency

The values of Total [Cl] in MSW, SRF and waste component categories derived from **Table 5-1** to **Table 5-3** are depicted in **Figure 5-1**. Boxplots of Total [Cl] in MSW, SRF and waste sub-fractions (component categories) as received reporting basis. Note: waste category *rubber-leather* was excluded due to data limitations and inconsistencies.. The boxplots of SRF and MSW are of a similar scale, but the interquartile range in MSW is wider than in SRF. This indicates a higher variability, which is also confirmed by the relative variation (CV) (**Table 5-1**). The relative variation of SRF is more than 30% lower than MSW.

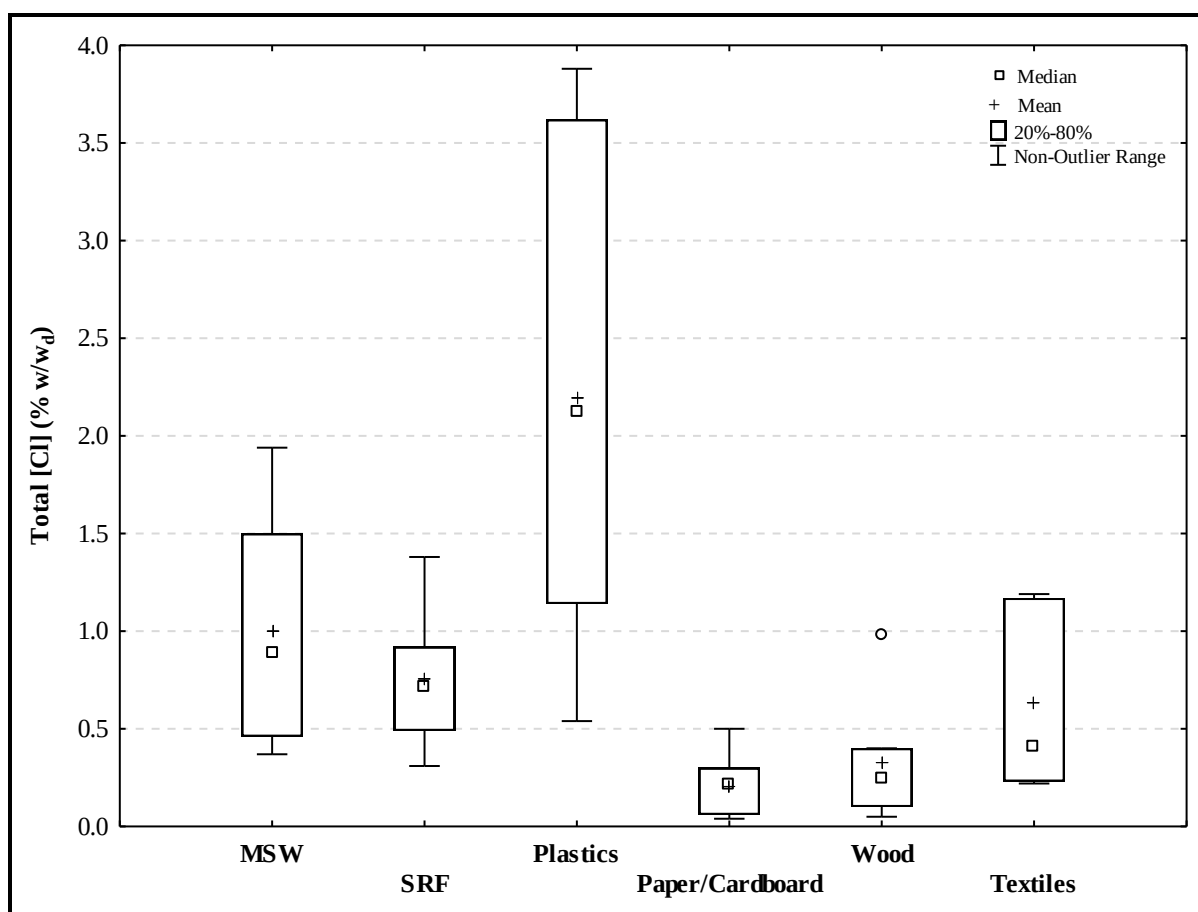


Figure 5-1. Boxplots of Total [Cl] in MSW, SRF and waste sub-fractions (component categories) as received reporting basis. Note: waste category *rubber-leather* was excluded due to data limitations and inconsistencies.

Regarding the waste component categories, the highest spread of [Cl] values was observed in *plastics*, while the lowest was in *paper/cardboard* (**Figure 5-1**). However, their relative variation (**Table 5-3**) is almost equal (with a relative variation nearly 53% for *plastics* and 52% for *paper/cardboard*) indicating similar relative Cl dispersion. The highest relative variation was found in *wood* probably

due to the extreme [Cl] value (0.98% w/w_d) presented in the boxplot, which increased relative variation from 56% to 88%. However, this value cannot be omitted, since considerable variation in [Cl] can be present depending on tree species (Pettersen R.C, 1984) and cross-contamination of such materials with chlorides through water absorption. Second in the descending order of [Cl] variability comes *textiles* (with a relative variation almost 65%). This might be related to the nature of this category, as *textiles* include both synthetic and natural fabrics leading to a variable [Cl]. A further division of this component category into sub-fractions may give a better estimation, but research preoccupation with *textiles* is not as great as with *plastics*. **Table 5-4** illustrates the Total [Cl] in sub-fractions of the *plastic* category, as defined by previous studies. These values were used to construct the dataset of *plastics* used in statistical analysis, as explained in **section 4.1.1.1**.

Table 5-4. Overview of Cl content in specific plastic categories or polymers.

SRF component	Total [Cl] (% w/w _d)	Reference
Packaging plastics	1.00	(Rotter et al., 2004)
Non-packaging films	0.60	
Other plastic products	8.50	
ABS	0.04	(Heikkinen et al., 2004)
HDPE	0	
PBT	0	
PET	0	
PP	0	
PVC	51.31	
Hard plastics (bottles and containers)	1.00	(Ma et al., 2010)
Soft plastics (bags and soft films)	0.60	
Non-packaging plastics	6.15	
Plastic carrying bags	2.51	(Chiemchaisri et al., 2010)
Other plastic bags	1.23	
Other plastics	3.95	
Durable plastic	0.02	(Velis, 2010)
Plastic film	1.28	
Other packaging	1.52	
Plastic (hard)	1.60	(Nasrullah et al., 2016)
Plastic (soft)	0.83	

5.1.2 Fate of Cl during SRF co-combustion in modern cement kilns

Figure 5-2 depicts the fate of Cl and the most prevalent forms of Cl during SRF co-combustion in modern cement kilns, accompanied by a generalised mass flow of typical Cl distribution. Cl behavior in a cement kiln has been examined by the application of WDF with high [Cl] and by the addition of Cl in raw meal, since Cl is introduced to the kiln through the raw materials and fuel (Saxena, 2003; Enders and Haeseli, 2011; Cortada Mut et al., 2015). Chlorine may either leave the system ('sinks') through the clinker, the baghouse dust and unburned chlorinated emissions in the stack or remain in the kiln ('stock'). Chlorine hardly leaves the kiln via clinker in modern cement kilns, due to its high volatility and the operating conditions (Holderbank, 1992). Exceptions can be explained mainly by the cooling down of sintering zone, Cl encapsulation in big material lumps, and/or formation of high internal Cl cycles (Holderbank, 1992; Schorcht et al., 2013).

Chlorine can be found in the clinker in the form of inorganic chlorides with the most prevalent being CaCl_2 (Cortada Mut et al., 2015). Chloride compounds, such as chlorellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$), HCl, Cl_2 , alkaline earth chlorides (e.g MgCl_2 , CaCl_2) and transition metal chlorides, can be found in the pre-heater zone (Sidhu et al., 2001; Saint-Jean et al., 2005).

Chlorellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3\text{Cl}_2$) can be formed in the preheater due to the reaction of HCl gas with the raw meal, and is affected by the degree of contact between the kiln gases and the cement kiln dust (CKD) (Saint-Jean et al., 2005). Chlorellestadite can also be found in build-ups and kiln rings; build-ups contain both organic and inorganic Cl compounds, with the most prevalent being chlorellestadite, KCl and NaCl (Bhatty, 2011).

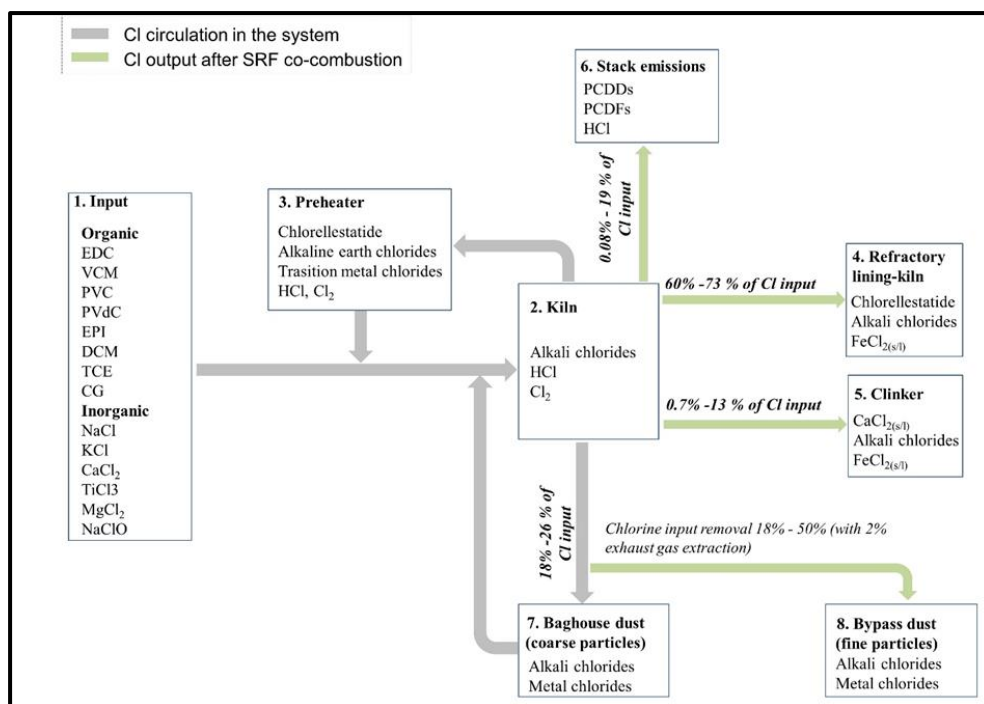


Figure 5-2. Most prevalent chloride compounds of SRF and their fate during co-combustion in a kiln-preheater system: Input chlorinated compounds present in SRF (1) are volatilized during combustion in the kiln (2) and are condensed in the preheater (3) forming a Cl circulation, by which Cl can remain in the kiln ('stock') (4); leave the system through the clinker (5) or as unburned chlorinated emissions in the stack (6); and concentrated in CKD: coarse particles are returned to the kiln (7) whereas fines can be removed from the system if bypass system installed (8).

5.1.2.1 Effects of Cl input on clinker quality

Chlorine primarily reacts with alkalis and the remainder (less than 1%) reacts with the free lime (CaO) contained in the raw meal, due to its stronger affinity with alkalis than calcium (Cortada Mut et al., 2015; Holderbank, 1992; Sutou et al., 1999). The remaining Cl is absorbed by the free lime forming $\text{CaCl}_{2(s/l)}$ (Sutou et al., 1999; Cortada Mut et al., 2015) (**Reaction 5-1**). This has a low melting point (772°C) such that, despite the low quantities, the raw meal becomes sticky (Vainikka et al., 2011). This phenomenon reduces the ability of raw meal to flow, causing operating problems in the system (Cortada Mut et al., 2015; Karstensen, 2006).



Kwon et al. (2005) investigated the effect of Cl on clinker quality by adding NH_4Cl to raw materials. Total [Cl] ranged from 0.5% to 2% w/w and the mineralogical composition of clinker was analyzed by X-ray diffraction. The results showed that Cl acted as an accelerator for the liquid-solid

clinkerization reaction, forming $\text{CaCl}_{2(s/l)}$ by reducing the amount of free lime and alite (C_3S) and increasing the amount of belite (C_2S) in the clinker. While some belite is welcome because of its ease of grindability (Maki et al., 1993), the destabilisation of alite is unwelcome since it is this phase, typically constituting 45-65% of the clinker, which makes the main contribution to strength, particularly at early ages (Talaber, 1982).

Based on a previous study, a mass substitution rate of 50% SRF in cement kilns may induce a fivefold increase in clinker chloride contents (Gendebien et al., 2003). Despite this, the chloride concentrations were still below typical limits for chloride in Portland cement, of $1000 \text{ mg Cl kg}^{-1}$ (0.1% w/w) (BS 197-1, 2000). This was due to complete Cl vaporization in the sintering zone induced by the high vapor pressure (Gendebien et al., 2003; Lechtenberg and Diller, 2012).

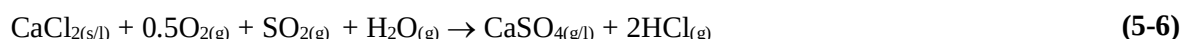
Despite the impact on clinker quality, CaCl_2 formation promotes Cl circulation. It can react with oxygen and water vapours producing Cl_2 and HCl , as follows (Shigapov et al., 1988):



In addition, CaCl_2 can form metal chlorides either with direct (**Reaction 5-4**) or indirect chlorination (**Reactions 5-5a and 5-5b**) at 1000°C (Chan and Kirk, 1999):



HCl can also be formed by the sulfation of CaCl_2 increasing the risk of corrosion of the steel wall (Cortada Mut et al., 2015):



5.1.2.2 *Effects of Cl input on flue gas*

HCl is formed during combustion of SRF in cement kilns (with formation starting from 200°C) (Lechtenberg and Diller, 2012), but the Total [Cl] in SRF is not critical regarding gaseous pollutants, due to the alkaline environment in the kiln (Genon and Brizio, 2008). Schorcht et al. (2013) reported data from continuous dust measurements in the clean gas of 253 kilns and found that HCl emissions from European cement kilns ranged from 0.02 to 20 mg Nm³, depending on the composition of raw materials and fuels, the age and design of the plant, and the requirements of the regulatory authority. Gendebien et al. (2003) reported that SRF use in cement kilns under 50% mass substitution can lead to an almost 24% increase in HCl emissions, which can be captured by the alkaline scrubber effect (Karstensen, 2006), while a 15% mass substitution rate does not affect the HCl emissions (Rovira et al., 2010). This statement is in agreement with Fyffe et al. (2012) who carried out burn tests of 130 tonnes of SRF fed into a precalciner with a 10% energy substitution rate, finding no increase in HCl emission rates.

Despite HCl emissions, other chlorinated organic compounds, such as PCDDs/Fs, can be formed in the presence of Cl (Karstensen, 2008). However, modern preheated cement kilns that use non-hazardous wastes as co-fuels present PCDDs/Fs emissions lower than 0.1 ng I-TEQ m⁻³ under well managed operation, indicating that waste can be used as co-fuels (Peters et al., 1983; Karstensen, 2008; Schorcht et al., 2013). Genon and Brizio (2008) reported that SRF does not affect the emissions of chlorinated-micropollutants due to the thermal conditions and alkaline environments in the kiln.

5.1.2.3 *Effects of Cl input on cement kiln dust*

According to the UK Environment Agency (2001), the majority of the Cl remains in the kiln, while a small part is precipitated with particulates in the de-dusting system. The volatile Cl is mainly concentrated in the fine particles of the CKD, produced by the exhaust gas cooling. The coarse dust particles are returned to the kiln (via injection into the raw feed or directly to the mill (Environment Agency, 2001)), while the fine particles, known also as Cl bypass dust, are treated as waste (Saito et al., 2011).

Specifically, heavy metals are vaporized and react with CaCl_2 forming unwanted metal chlorides (**Reactions 5-4 and 5-5**) through the sintering process, which are concentrated within the CKD in the bag filter (Zhang et al., 2018a; Miura et al., 2001). The most prevalent chloride salts during SRF co-combustion are the strong hydration retarders PbCl_2 and ZnCl_2 (Vainikka et al., 2011), since Pb is used as a metal stabilizer in plastics, textiles and leather and Zn as acid scavenger and filler in plastics (Zweifel et al., 2009).

When increasing quantities of Cl bypass dust are produced, it becomes difficult to recover all of the Cl, necessitating the installation of a bypass system (Sutou et al., 1999; Enders and Haeseli, 2011; Cortada Mut et al., 2015). As a rule of thumb, the [Cl] input has to be less than 400 g tn^{-1} clinker, otherwise a bypass system is required (Lechtenberg and Diller, 2012). The system consists of a probe which extracts and cools the exhaust gas, a cyclone which separates and returns coarse dust to the kiln, and a bag filter or electrostatic precipitator which captures the bypass dust and the exhaust gas. Although the bypass system offers a technical solution for Cl removal, additional capital cost and energy consumption is required (Enders and Haeseli, 2011). Besides, the disposal of bypass dust is difficult due to environmental restrictions (Lechtenberg and Diller, 2012). Sutou et al. (1999) reported that extraction of 2% and 5% of kiln exhaust gas (bypass ratio) could lead to nearly 50% and 90% Cl removal, respectively. A more recent study found that Cl removal from the system was nearly 18% with a 2% bypass ratio (Zhan et al., 2016).

Considering the literature evidence on the sources of Cl in SRF (**Section 2.4.3.1**) and related implications in cement kilns (**Section 2.4.3.2**) along with the critical analysis on the fate of Cl during SRF co-combustion, a general overview can be visualized in **Figure 5-3** indicating the prevalent forms of Cl in SRF during pre- and co-processing in cement production and how this can affect the operation of the kilns.

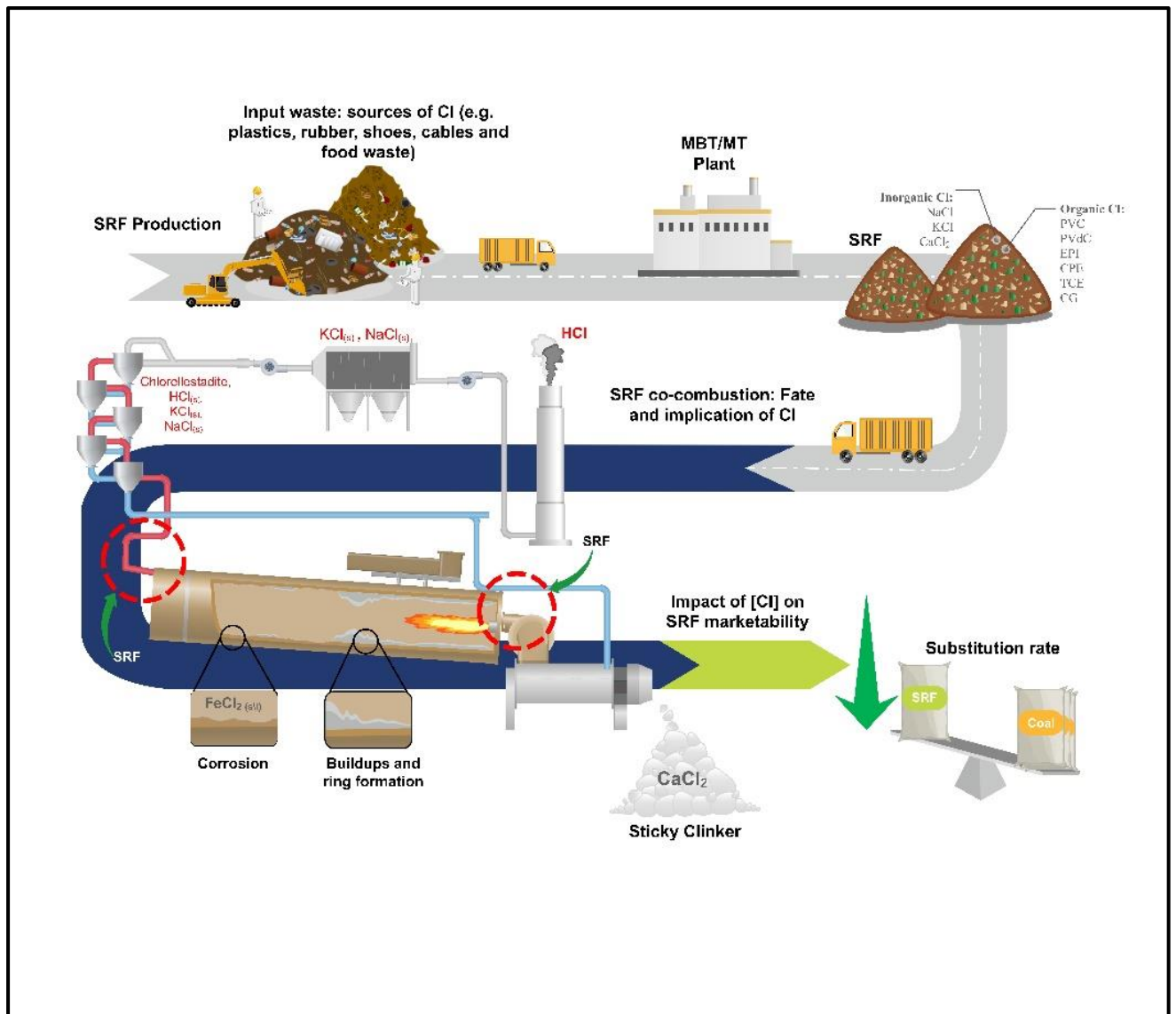


Figure 5-3. Overview of sources, fate and implications of Cl in SRF when co-combusted in cement kilns (designed in EdrawMax software).

5.2 Quantification of typical content of prevalent SRF polymers in waste categories

At this section the results obtained from literature review in relation to the content of prevalent SRF polymers in waste MCP waste categories (**Section 4.1.2.1**) are presented. The results of this section constituted the basis for: i) the formulation of the design region using them as upper and lower bounds for the construction of complex constraints (**Table 4-6**); and ii) the determination of content of

biopolymer in the waste mixtures of the hold-out validation set so that to assess the hold-out validation error for biopolymers, addressing the research objective (**O4**).

Biopolymers content analysis of SRF/RDF

In **Table 5-5**, typical ranges of biopolymers (cellulose, hemicellulose, and xylan) content for four main biomass waste item categories of MSW (therefore found also in SRF/RDF) are summarised: i) *paper/cardboard*; ii) *wood*; iii) *non-wood biomass* materials used in papermaking; and iv) *natural fibers* mainly used in the textile industry, as reported in **Section 2.4.1.1**. The specific products associated with these item categories can either be found directly in SRF/RDF (e.g. newspapers in the item category of *paper/cardboard*) or affect the biomass content in SRF/RDF through their presence in the manufacturing process of prevalent waste items (e.g. straw or hemp in the category of *non-wood biomass* for papermaking).

Table 5-5. Typical content of biopolymers – cellulose, hemicellulose and lignin – for four main biomass waste item categories present in MSW: *paper/cardboard*; *wood*; *non-wood biomass* materials used in papermaking; and *natural fibers* mainly used in the textile industry, as received reporting basis.

Biomass material		Cellulose (% w/w)	Hemicellulose (% w/w)	Lignin (% w/w)	References
Paper	Laser printed paper	> 90	3.2		(Casillas et al., 2018)
	Newspaper	38-68	9-40	18-30	(Derkacheva and Tsyppkin, 2018; Vukoje and Rožić, 2018; Sun and Cheng, 2002; Ioelovich, 2013)
	Copy paper	46-77	12-21	1-2	(Ma et al., 2016; Vukoje and Rožić, 2018)
	Cardboard	57-60	11-21	10-18	(Sørum and Task, 2001; Ma et al., 2016; Vukoje and Rožić, 2018; Ioelovich, 2013)
	Office paper	60-85	4-12	1-2	(Vukoje and Rožić, 2018; Ioelovich, 2013)
	Coated paper	42	9	24	(Vukoje and Rožić, 2018)
Abaca		56-63	11-25	7-9	(Dufresne, 2012; Liu et al., 2018)

Biomass material		Cellulose (% w/w)	Hemicellulose (% w/w)	Lignin (% w/w)	References
Non-wood materials for pulping	Bamboo	52-68	15-26	21-31	(Liu et al., 2018)
	Baganese	37-55	17-32	18-25	(Dufresne, 2012; Liu et al., 2018; Ioelovich, 2013)
	Cornstalk	35-38	24-38	18-20	(Liu et al., 2018; Ioelovich, 2013)
	Hemp	57-77	9-15	5-10	(Dufresne, 2012; Liu et al., 2018)
	Kenaf	53 -72	20-23	9-18	(Dufresne, 2012; Liu et al., 2018)
	Reed	42-50	20-23	22-25	(Liu et al., 2018)
	Rice straw	28-36	23-28	12-16	(Liu et al., 2018)
	Wheat straw	29-45	15-35	12-21	(Dufresne, 2012; Liu et al., 2018; Ioelovich, 2013; Wang, 2013)
Natural textile fibers	Cotton (white & brown)	83-97	1-6	< 1	(Dufresne, 2012; Liu et al., 2018)
	Jute	57-71	12-26	12-26	(Dufresne, 2012; Liu et al., 2018; Hao et al., 2018; Dufresne, 2008)
	Flax	64-88	6-21	2-25	(Dufresne, 2012; Liu et al., 2018; Dufresne, 2008; Hao et al., 2018; Ioelovich, 2013; Phyllis, 2020)
	Sisal	43-66	12-24	8-10	(Dufresne, 2012; Liu et al., 2018; Hao et al., 2018; Dufresne, 2008)
	Ramie	69-76	13-16	<1	(Dufresne, 2012; Hao et al., 2018; Dufresne, 2008)
Wood materials	Softwood	35-50	20-35	25-35	(McKendry, 2002; Sun and Cheng, 2002; Ioelovich, 2013; Phyllis, 2020; Brebu and Vasile, 2010)
	Hardwood	40-55	20-40	16-25	
Furniture wood waste		43-47	20-22	32-34	(Moreno and Font, 2015)
Typical softwood	Spruce	41-49	21-27	28-29	(Sørum and Task, 2001; Heikkinen et al., 2004; Phyllis, 2020)
	Pine	38-50	24-30	25-30	(Sørum and Task, 2001; Phyllis, 2020)
Typical hardwood	Birch	45-48	25-39	19-24	(Sørum and Task, 2001; Phyllis, 2020)

Biomass material	Cellulose (% w/w)	Hemicellulose (% w/w)	Lignin (% w/w)	References
Beech	48-49	22-28	24	(Phyllis, 2020)
Eucalyptus	44-48	21-32	25	(Phyllis, 2020; Klash et al., 2010)
Oak	45	20	25	(Phyllis, 2020)
Poplar	41-49	17-33	18-26	(Phyllis, 2020)

The typical ranges of biopolymers from **Table 5-4** are depicted in **Figure 5-4**. The presence of extreme values observed in **Figure 5-4**, indicates the considerable heterogeneous composition of biomass materials that can be present in SRF/RDF. *Paper/cardboard* and *natural fibers* contain higher content of cellulose compared to *wood* and *non-wood biomass* (Watkins et al., 2015) due to the delignification process in papermaking (Viikari et al., 2009) and the need of textile industry to use fibers with high absorbency and whiteness (Jia et al., 2018), respectively.

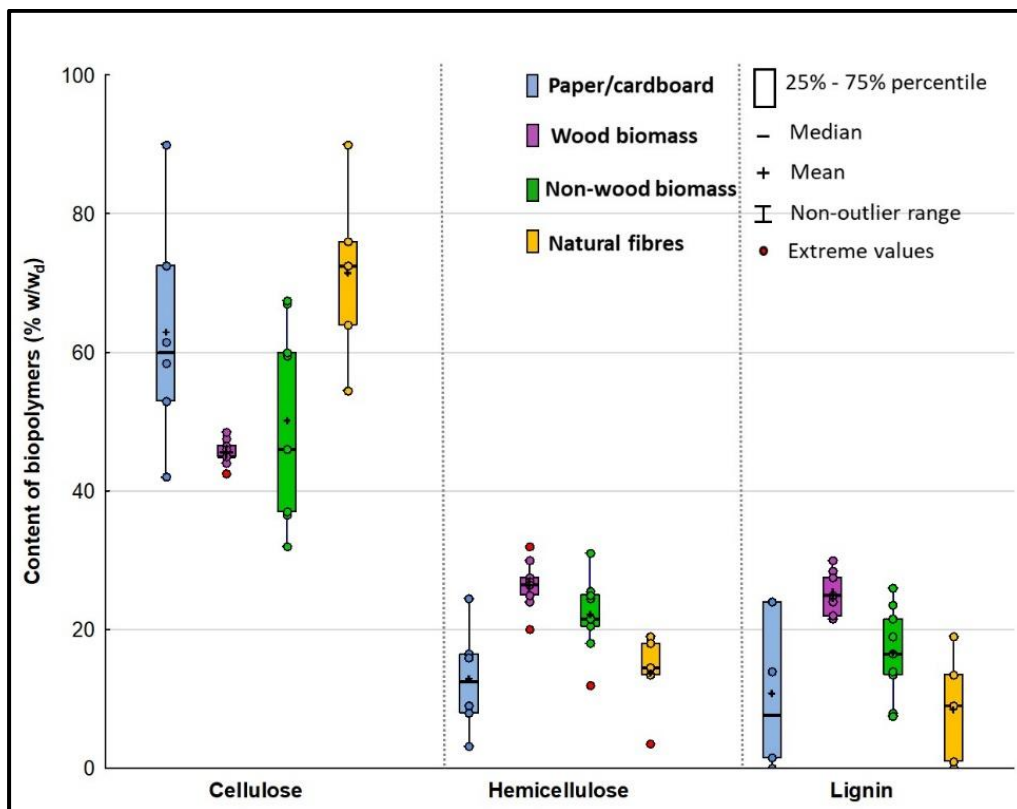


Figure 5-4. Typical content (dry basis) of biopolymers – cellulose, hemicellulose and lignin – for four main biomass waste item categories present in MSW indicating the variable content of biopolymers in the biomass fraction of SRF/RDF depending on the source (between and within biomass waste item categories): *paper/cardboard*; *wood*; *non-wood biomass* materials used in papermaking; and *natural fibres* mainly used in the textile industry. Non-outlier range defined as ≤ 1 interquartile range (IQR). Extreme values defined as ≤ 1.5 IQR.

The calculation of confidence intervals (LCI-UCI, $\alpha=0.1$) using the data of **Figure 5-4**, showed that the biomass waste item category of *paper/cardboard* contains cellulose in the range of 49.2-76.6% w/w_d (mean: 62.9% w/w_d), 6.6-19.1% w/w_d (mean: 12.9% w/w_d) hemicellulose and 1.5-20.2% w/w_d (mean: 10.8% w/w_d) lignin ($\alpha=0.1$). Similarly, *wood* contains 44.4-46.7% w/w_d (mean: 45.6% w/w_d) cellulose, 24.2-28.5% w/w_d (mean: 26.3% w/w_d) hemicellulose and 23.1-26.9% w/w_d (mean: 25% w/w_d) lignin ($\alpha=0.1$). The ranges of cellulose, hemicellulose and lignin fluctuated in a range of 58.7-84.1% w/w_d (mean: 71.4% w/w_d), 7.8-19.6% w/w_d (mean: 13.7% w/w_d) and 0.8-16.2% w/w_d (mean: 8.5% w/w_d) for *natural fibers* and 41.7-58.6% w/w_d (mean: 50.2% w/w_d), 18.9-25.5% w/w_d (mean: 22.2% w/w_d) and 12.6-20.6% w/w_d (mean: 16.6% w/w_d) for *non-wood biomass* ($\alpha=0.1$), respectively. The content of biopolymers for the *wood* item category has a narrower range compared to this of *paper/cardboard*. This difference can also be seen in **Figure 5-4** as the interquartiles of *paper/cardboard* are relatively wide, whereas the interquartiles of *wood* are the narrowest.

Fossil-based plastics content analysis of SRF/RDF

In **Table 5-6**, an indicative content of prevalent fossil-based plastic polymers that can be present in SRF/RDF arising from typical contents of these plastic polymers in the overall plastics production and plastic waste arisings is presented. These indicative contents from **Table 5-6** are statistically visualized in **Figure 5-5**.

Table 5-6. Typical content of prevalent fossil-based plastic polymers – PE, PP, PET and PVC – in overall plastics production and plastics waste arisings as received reporting basis.

Composition in plastic fraction (%)					Year	Stage of the supply chain	Reference
PE	PP	PET	PVC	Others			
37	25	9	18	11	2012	Production	(Shamiri et al., 2014)
38	22	15	4	21		End of life	(WRAP, 2009)
31	18	9	10	32	2014	Production	(Yeo et al., 2018)
29	19	6	12	34	2010	Production	(Villanueva and Eder, 2014)
42	14	10	6	28	Typical	End of life	(Bodzay and Bánhegyi, 2016)
30	19	8	10	33	2016	Production	(PlasticsEurope, 2019a)
36	21	9	12	22	Typical	Production	(Geyer et al., 2017)
51	19	16		14	2010	Production (of plastic packaging)	(Villanueva and Eder, 2014)

Figure 5-5 shows that PE is by far the dominant polymer in the plastic fraction of SRF/RDF (32-43% w/w, $\alpha=0.1$) followed by PP (17-22% w/w, $\alpha=0.1$), PET (8-13% w/w, $\alpha=0.1$), PVC (6-14% w/w, $\alpha=0.1$) and other plastics including fossil-based and bio-based plastic polymers (17-30% w/w, $\alpha=0.1$).

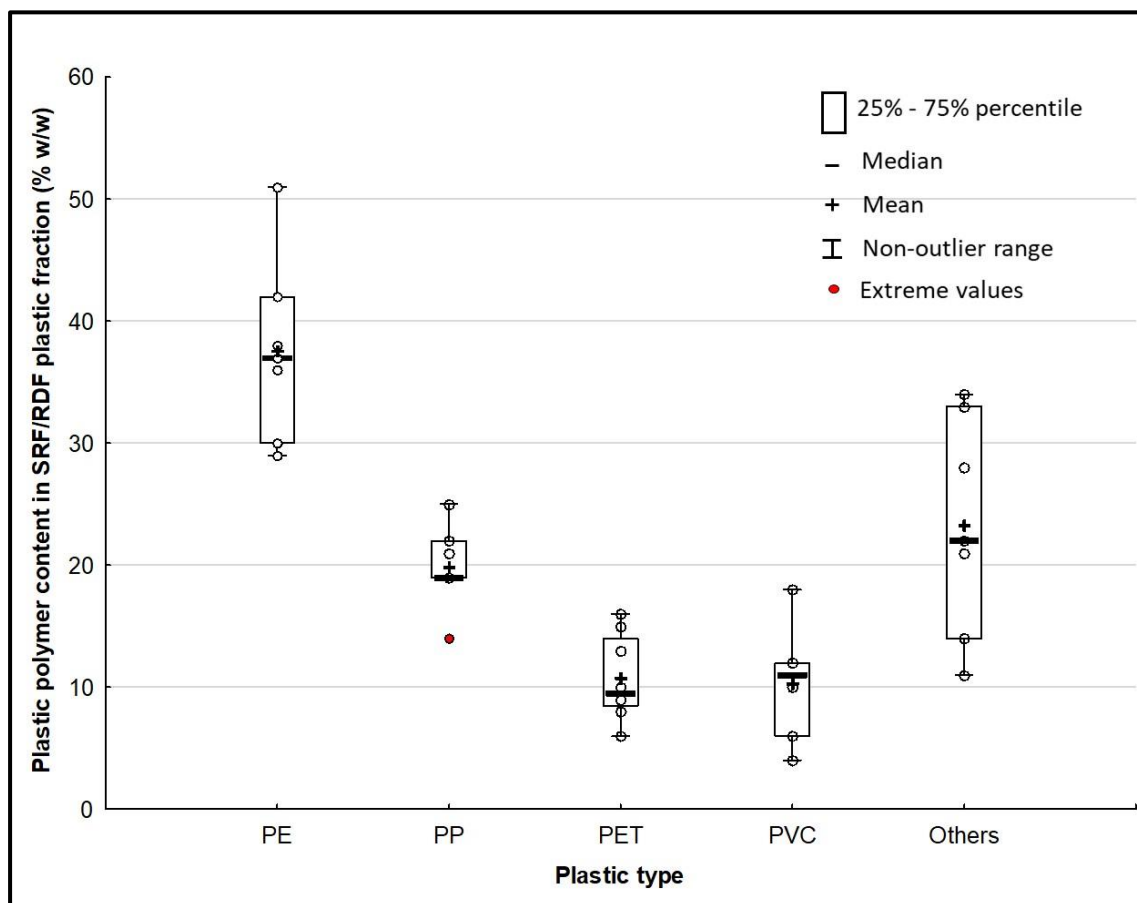


Figure 5-5. Typical content of fossil-based plastic polymers in overall plastics production and plastics waste arisings denoting an indicative content of the most prevalent plastic polymers in SRF/RDF: PE, PP, PET and PVC. Non-outlier range defined as ≤ 1 interquartile range (IQR). Extreme values defined as ≤ 1.5 IQR.

5.3 Prevalent experimental conditions in TGA of waste-derived materials

At this section the results obtained from literature review in relation to the most common operating conditions applied in TGA experiments for compositional analysis of waste-derived materials (Section 4.1.2.2) are presented. The results of this section constituted the basis for the selection of operating conditions applied in TGA experiments for both uncertainty quantification for TG-DTG (O3) and ML model development (O4).

Table 5-7 provides conditions used in *non-isothermal* TGA experiments for the investigation of thermal behaviour of waste-derived materials by previous researchers.

Table 5-7. Experimental conditions applied in TGA experiments for determination of thermal behaviour of MSW, SRF/RDF and other waste items/materials under *non-isothermal* conditions as received reporting basis.

Material	Heating rate (°C)	Sample mass (g)	Maximum temperature (°C)	Atmospheric conditions	Reference
SRF	20	5	1000	Inert	(Aleksandra and Wojciech, 2018)
	5, 10, 15			Oxidative & Inert	(Conesa and Rey, 2015)
	5			Oxidative	(Medic-Pejic et al., 2016)
	10			Oxidative	(Chae et al., 2019)
RDF	10	30	950	Oxidative	(Akdağ et al., 2016)
RDF	10		600	Inert	(Edo et al., 2016a)
	10		850	Inert	(Stępień et al., 2019)
	10		800	Inert	(Efika et al., 2015)
	25		800	Inert	(Robinson et al., 2016)
	20		1000	Inert	(Skodras et al., 2009)
	10		800	Inert	(Bosmans et al., 2014)
	20			Inert	(Tokmurzin et al., 2019)
	10		1000	Oxidative	(Chen et al., 2018)
	15		900	Inert	(Seo et al., 2010)
	10		800	Inert	(Dantias and Liodakis, 2018)
	5, 10, 20, 50		900	Inert	(Casu et al., 2006)
	3, 5, 7, 9		550	Inert	(Lin et al., 1999)
	5, 10, 15, 20, 25, 30, 40, 50		900	Inert	(Çepelioğullar et al., 2016)
RDF & MSW	10, 20, 30, 40		1000	Inert	(Azam et al., 2019)
	10			Inert	(Cozzani et al., 1995)
	20		1000	Oxidative & Inert	(Grammelis et al., 2009)
	10	5	600	Inert	(Porshnov et al., 2018)
	10	20	650	Inert	(Silva et al., 2015)
RDF & plastic waste	25	17.5	900	Inert	(Singh et al., 2012)
MSW components	10		800	Oxidative & Inert	(Wagland et al., 2011)
	20	5	550	Inert	(Heikkinen et al., 2004)

Material	Heating rate (°C)	Sample mass (g)	Maximum temperature (°C)	Atmospheric conditions	Reference
	5		800	Oxidative	(Boumanchar et al., 2017)
	20	5.5	800	Inert	(Gug et al., 2015)
	10	10		Oxidative	(McGhee et al., 1995)
	10	15	590	Inert	(Sørsum et al., 2001)
	30	10	700	Inert	(Chhabra et al., 2019)
	10		1000	Inert	(Chen et al., 2015b)
	10			Inert	(Cheng et al., 2007)
	10		1000	Inert	(Zhou et al., 2015)
	20		900	Inert	(Ma et al., 2019)
	5, 20, 100			Inert	(Skreiberg et al., 2011)
Wood waste	2, 5, 10, 15		700	Inert	(Słopiecka et al., 2012)
	5, 10, 20		900	Inert	(Moreno and Font, 2015)
	10, 20, 30		900	Inert & Oxidative	(Yurdakul and Atımtay, 2015)
	10		1000	Oxidative	(Kuznia and Magdziarz, 2013)
Textile waste	1, 5, 10, 20, 40, 60		1000	Inert	(Miranda et al., 2007)
Plastic waste	10, 20, 30, 40	1.25	800	Inert	(Park et al., 2012)
	5, 10, 20, 40		700	Inert	(Silvarrey and Phan, 2016)
	10		900	Inert	(Yang et al., 2001)

Figure 5-6 obtained by **Table 5-7** indicates that studies interested in the thermal degradation of SRF/RDF selected inert atmosphere, whereas studies interested in the combustion behaviour selected oxidative conditions (air or oxygen): the majority of the studies (76%) selected an inert atmosphere, using mainly nitrogen. Few researchers applied both atmospheres to draw comparisons (Grammelis et al., 2009; Skodras et al., 2009; Edo et al., 2016a; Conesa and Rey, 2015). Nearly 55% of total TGA experiments of waste-derived materials was conducted using a heating rate of 10°C min⁻¹ or less, with a view to obtaining a comparatively better resolution of the decomposition profile of the samples.

Despite the inherent heterogeneity of SRF/RDF, 55% of studies selected a sample mass ≤ 10 mg, whereas only one study (5% of total number) selected 30 mg. However, it is worth noting that most of the studies (56%) omitted to report the sample mass used in the TG experiments. **Figure 5-6** shows that 24% of the total studies selected a temperature range starting from room temperature and ending

between 550-750 °C, whereas the majority of researchers (51%) selected a maximum temperature ranging between 750-950 °C.

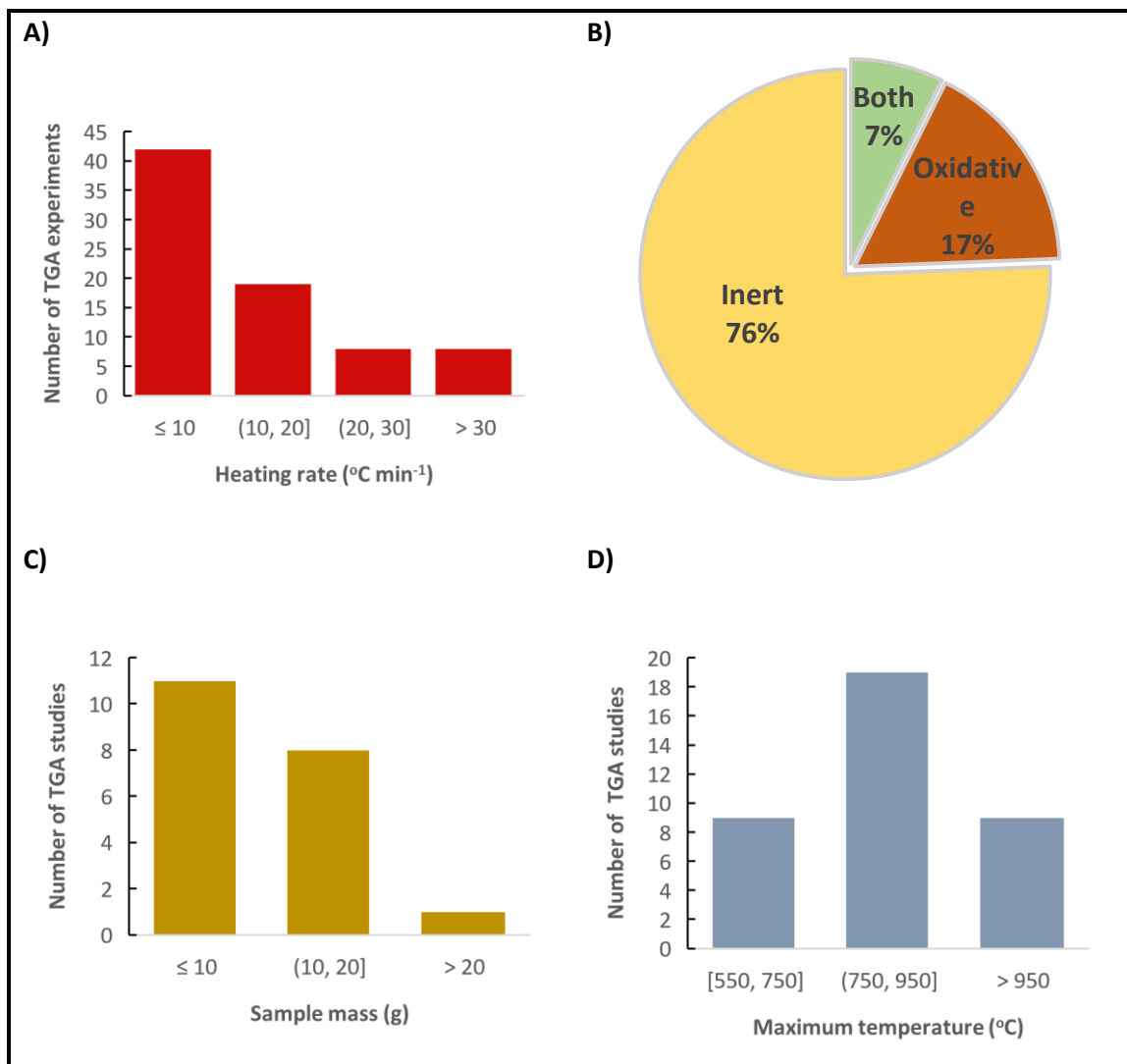


Figure 5-6. Non-isothermal conditions applied in TGA experiments for the investigation of thermal behaviour of MSW, SRF/RDF and several waste items/materials as received reporting basis indicating the typical experimental conditions used in TGA compositional analysis of SRF/RDF: **A)** selected heating rates per TGA experiment; **B)** selected atmospheric condition per study; **C)** selected sample mass per study; and **D)** selected maximum temperature per study.

5.4 Establishment of fitness-for-purpose sub-sampling plan for SRF characterization

At this section the results obtained from the assessment of sample preparation scenarios based on ToS-formula for the establishment of a fitness-for-purpose sub-sampling plan for SRF characterization by implementing DoE1 (**Section 4.2**) is presented, addressing the research objective (O2).

5.4.1 Beneficial effects of shredding based on ToS

5.4.1.1 Effect of cryomill settings on fundamental error

Table 5-8 presents common metrics of PSD, such as d_{90} , d_{50} , d_{10} and span, generated by cryomill, which were used to statistically compare four different shredding programs. Specifically, d_{90} of P4, P5 and P9 ranges between 110-152 μm , and it is more than twice larger for P2 (356 μm). ANOVA test showed statistical difference amongst the cryomill programs regarding all PSD metrics (d_{10} , d_{50} , d_{90} and span). In addition, post hoc tests showed that all shredding programs statistically differ from each other. ANOVA results, post hoc tests and the required key assumptions are provided in **Appendix C2**. However, **Figure 5-7**, which illustrates the cumulative PSD for SRF particles after cryogenic shredding under these four shredding programs, indicates that shredding programs achieved similar PSD except for P2.

Table 5-8. PSD metrics for SRF particles generated by four different configuration setting of secondary shredding (cryomill).

PSD metrics	P9	P5	P4	P2
d_{10} (μm)	3.5	3.5	4.2	6.2
d_{50} (μm)	25.7	29.7	35	82.9
d_{90} (μm)	110	141	152	356
Span (%)	4.16	4.61	4.24	4.21

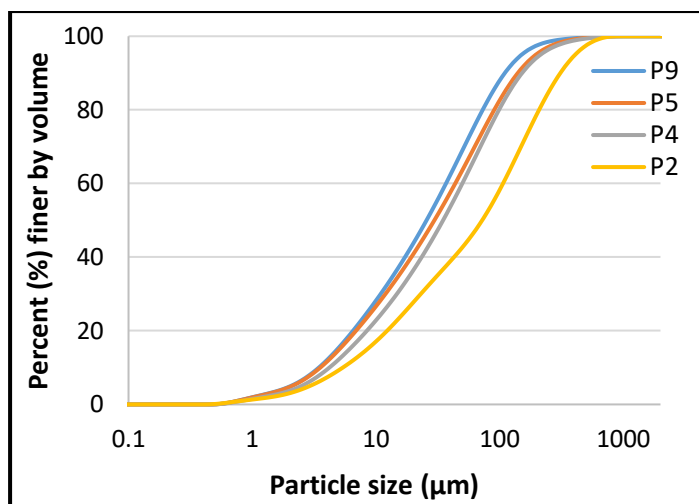


Figure 5-7. Cumulative PSD for SRF particles shredded by cryomill under 4 different shredding programs.

The theoretical model of ToS (**Eq. 2-3**) showed that configuration settings of cryomill do not considerably affect the overall sub-sampling uncertainty (**Figure 5-8**). It was found that the overall FE (arising from the overall sub-sampling process) is identical for P9, P5 and P4 (33.6%), whereas for P2 a negligible rise is observed (33.8%). Considerable difference can be found only in the FE arising only from the final stage of sub-sampling, from test sub-sample (7 g) to test portion (0.3 g). The highest difference is between P9 (0.3%) and P2 (3.2%), where the FE increases more than ten times at the final sub-sampling stage. Amongst these four cryomill programs (**Section 4.2.2**), P4 with four grinding cycles was selected as it is the best combination of sample homogeneity (low FE), cost and time savings (lower number of grinding cycles compared to P5 with five cycles and P9 with nine cycles).

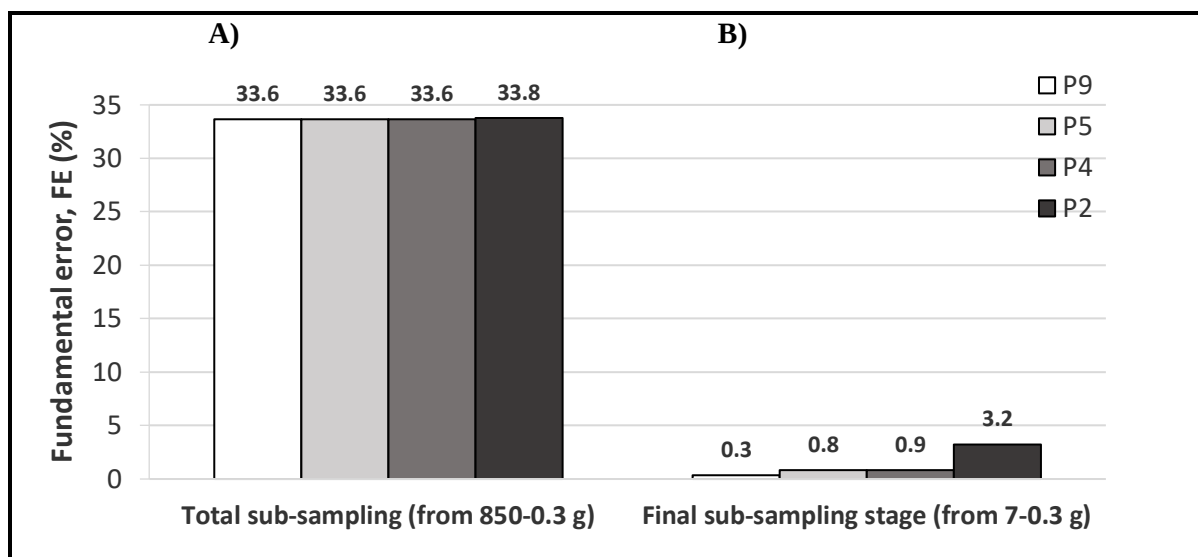


Figure 5-8. Fundamental error (FE) arising from the sub-sampling plan applied for the determination of Total [Cl] in SRF after shredding of test sub-samples with cryomill (secondary shredding) under four different configuration settings based on ToS: **(A)** overall FE during sub-sampling from the sample (850 g) to test portion (0.3 g); and **(B)** FE during the final stage of sub-sampling from the test sub-sample (7 g) to test portion.

5.4.1.2 Trend of FE under different shredding scenarios: Nomographs

Nomographs constructed for the three different shredding scenarios: sub-sampling without shredding (NS), sub-sampling with primary shredding (PS), and current sub-sampling plan (CS) (**Figure 5-9**), as described in **Section 4.2.4**. The points of nomographs (A to H) indicate the alteration of mass and particle size of sub-samples during sub-sampling based on the three scenarios. The movement from one point to another indicates the stages of shredding and riffle splitting. For example, the sample was split into two sub-samples from point A to B (from 850 g to 425 g), the sub-samples were shredded with the cutting mill (primary shredding) from point B to D, consecutive stages of riffle splitting took

place from point D to E, and so on.

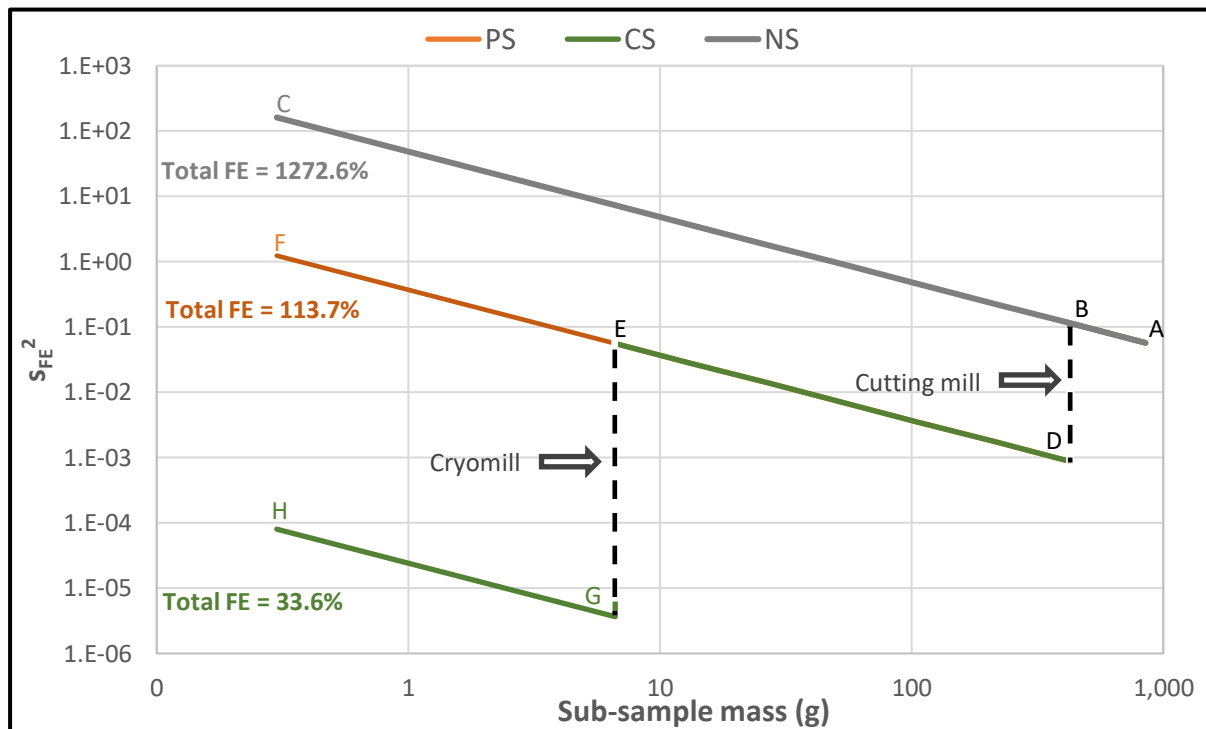


Figure 5-9. Trend of the variance of fundamental error (s_{FE}^2) during sub-sampling (nomograph) for the determination of Total [CI] in SRF under three shredding scenarios calculated by recasting the ToS-formula (Eq. 2-3): NS -sub-sampling without shredding (A-B-C); PS – sub-sampling with primary shredding (A-B-D-E-F); CS – the current sub-sampling plan including both primary and secondary shredding (A-B-D-E-G-H). The points above the trend lines demonstrate the mass and the particle size alteration of sub-samples during sub-sampling. The movement from one point to another indicate the stages of sub-sampling. Dotted black lines indicate the stages of shredding (primary with cutting mill and secondary with cryomill). Calculations for the construction of nomographs are given in **Appendix C3**.

For the three scenarios the process from point A to B is identical as shredding took place after the first stage of rifle splitting, while scenarios PS (points A-B-D-E-F) and CS (points A-B-D-E-G-H) are identical from point A (from sample of 850 g) to D (test sub-sample of ca. 7 g) as secondary shredding applied after the obtainment of the final sub-sample. The calculations conducted for the construction of nomograph (**Figure 5-9**) and the estimation of FE arising from each sub-sampling stage are presented in **Appendix C3**.

5.4.2 Adverse effects of shredding: *incorrect* sampling practices

5.4.2.1 Moisture evaporation during shredding

The moisture evaporation during shredding may lead to the miscalculation of residual MC and therefore of Total [CI] expressed on a dry basis. Based on the ANOVA test (**Appendix C4**), the null hypothesis that shredding processes (primary and secondary) do not affect the MC cannot be rejected. Similarly, **Figure 5-10** shows that residual MC is not affected by the shredding processes, although a negligible decrease after primary shredding with cutting mill is observed. There is a slight increase in residual MC after secondary shredding (cryomill). These insignificant differences of residual MC amongst the shredding stages can be attributed to SRF inherent heterogeneity. The test sub-samples for each shredding stage were drawn from the same sub-sample, but they were not identical.

Analytical measurements can be found in **Appendix C4**.

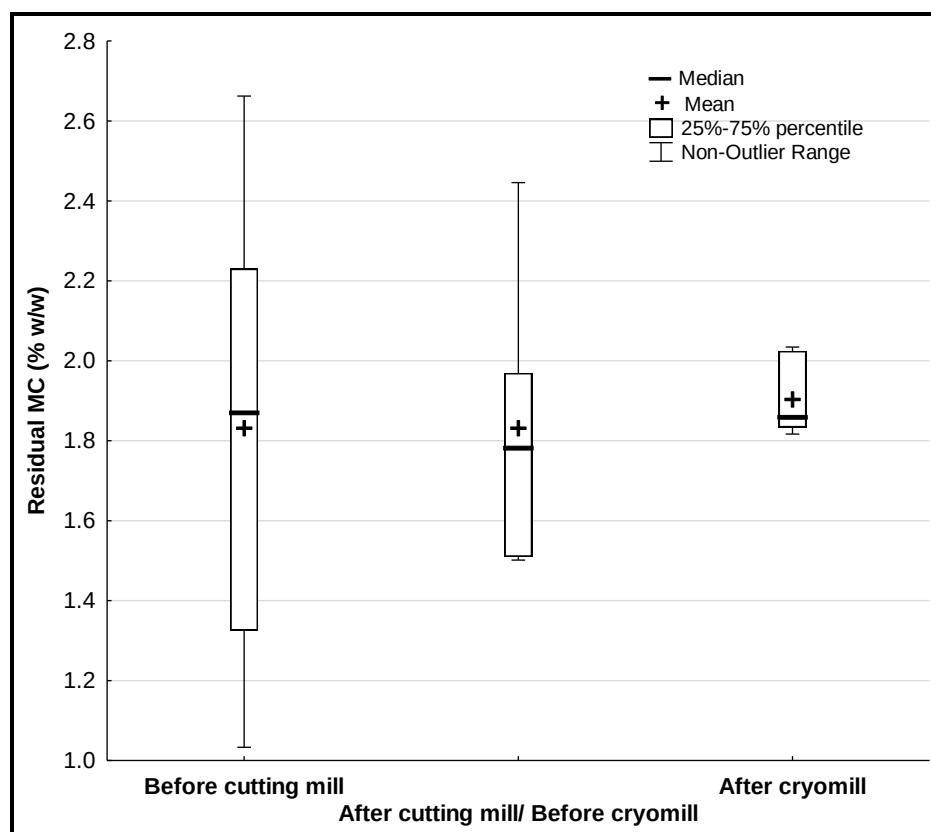


Figure 5-10. Residual MC in test sub-samples obtained by an SRF sub-sample of 50 g before and after two shredding processes: primary with the use of cutting mill and secondary with the use of cryomill.

5.4.2.2 Loss of sample mass during sub-sampling

Figure 5-11 shows the loss of sample mass induced at each stage of the sub-sampling process (riffle splitting and shredding). The loss of sample mass is 0.7% w/w mainly due to the considerable fraction of fines in SRF. The first stage of riffle splitting, that took place before primary shredding, induced 72% of the total mass loss (4.28 g out of 5.97 g) during the sub-sampling. At this stage of mass splitting, the range of particle size and the sample mass are maximum making sample handling more difficult. Primary shredding contributes nearly 10% to the total mass loss which corresponds to 0.07% w/w of total sample mass, whereas no loss occurs during secondary shredding.

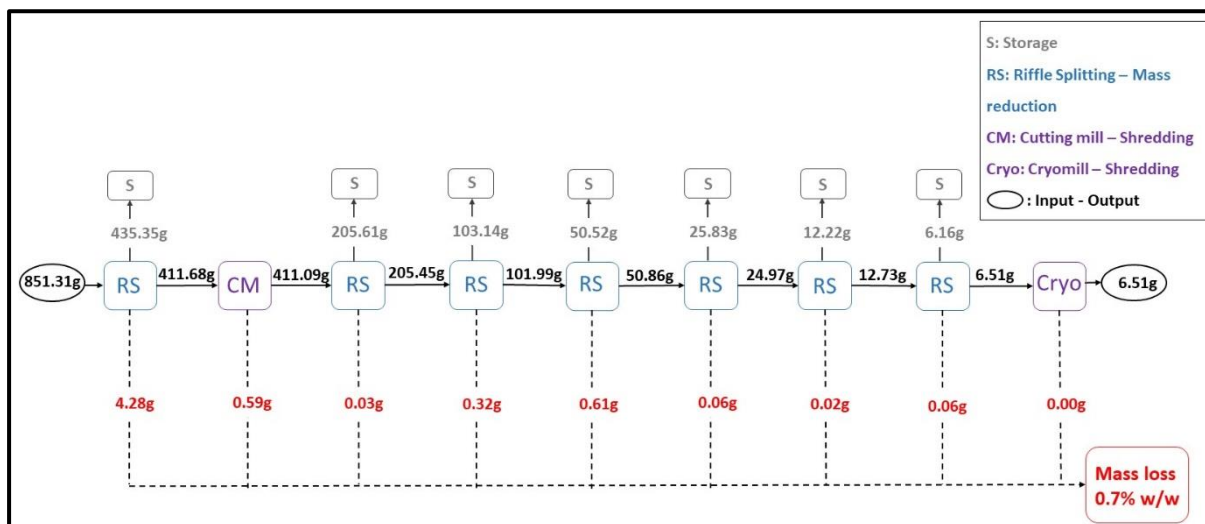


Figure 5-11. Mass flow analysis of SRF sample (ca. 0.85 kg), expressed in grams, during the sub-sampling process that consists of consecutive steps of mass reduction (riffle splitting) and two shredding stages (by using cutting mill and cryomill) for the obtainment of a test sub-sample (ca. 7 g).

5.4.2.3 Recovery of Cl from cryogenically shredded sub-samples

The recovery (*R*) of Total [Cl] from synthetic mixtures accounts for a range between 98.0 to 98.6%

(**Table 5-9**). The analytical values of Total [Cl] in SRF sub-samples were corrected based on **Eq. 4-2**

by taking the average of the recoveries from both synthetic mixtures.

Table 5-9. Recovery of Total [Cl] from synthetic mixtures with assigned Total [Cl] resembling SRF composition using BC combined with Palintest Chloridol analytical method.

SRF components	Synthetic SRF 1			Synthetic SRF 2		
	Composition (%) w/w) ¹	Assigned Total [Cl] (%) w/w)	Observed Total [Cl] (%) w/w) ²	Composition (%) w/w)	Assigned Total [Cl] (%) w/w)	Observed Total [Cl] (%) w/w) ²
Cellulose	33.81	0		34.33	0	
Xylan	4.02	0		4.05	0	

SRF components	Synthetic SRF 1			Synthetic SRF 2		
	Composition (% w/w) ¹	Assigned Total [Cl] (% w/w)	Observed Total [Cl] (% w/w) ²	Composition (% w/w) ¹	Assigned Total [Cl] (% w/w)	Observed Total [Cl] (% w/w) ²
Lignin	17.08	0		15.02	0	
HDPE	14.70	0		15.02	0	
PP	22.14	0		21.32	0	
PET	7.11	0		7.63	0	
PVC	1.15	53.71		2.64	53.71	
Total	100	0.62	0.61	100	1.42	1.39
Recovery (%)³			98.58			98.03

¹The composition of the mixtures was based on literature evidences (Heikkinen et al., 2004; Cuperus et al., 2005); ²The value derived from the arithmetic mean of three replicates; ³Eq. 4-2.

5.4.3 Fitness-for-purpose of sub-sampling plan based on ToS: Representativeness of test sub-samples

Figure 5-12 shows the measurement precision (95% confidence interval error bars of mean values from replicate measurements) and the dispersion (boxplots) of the 16 test sub-samples obtained for the determination of Total [Cl] and MC. The dotted red lines indicate the arithmetic mean of Total [Cl] (1.08% w/w_d) and MC (16.7% w/w) derived from the 16 test sub-samples. **Figure 5-12** provides an overview for the risk to obtain non-representative results based on ToS for the determination of SRF properties with higher (e.g. Cl) or lower (e.g. moisture) variability.

Assuming that the average values of 16 measurements represent the actual Total [Cl] and MC in the initially obtained SRF sample, then the potential to over- or under-estimate the critical component in the sample is present by drawing one test sub-sample. For example, the selection of the 4th sub-sample with the highest Total [Cl] (1.38% w/w_d) would overestimate the Total [Cl] in the sample (1.08% w/w_d) by 27.6%, whereas the 14th sub-sample with the lowest value (0.90% w/w_d) would underestimate the Total [Cl] by 16.4%. However, the majority of the test sub-samples does not differ from the mean value more than 15% except from the 7th (19.9% overestimation), the 4th (27.6% overestimation) and 14th (16.4% underestimation) sub-samples. Percentage differences of each test

sub-sample from the mean values of Total [Cl] is presented in **Table 5-10**. The difference between the minimum and maximum value leads to a range of 0.48% w/w_d, which is equal with a relative range 44%.

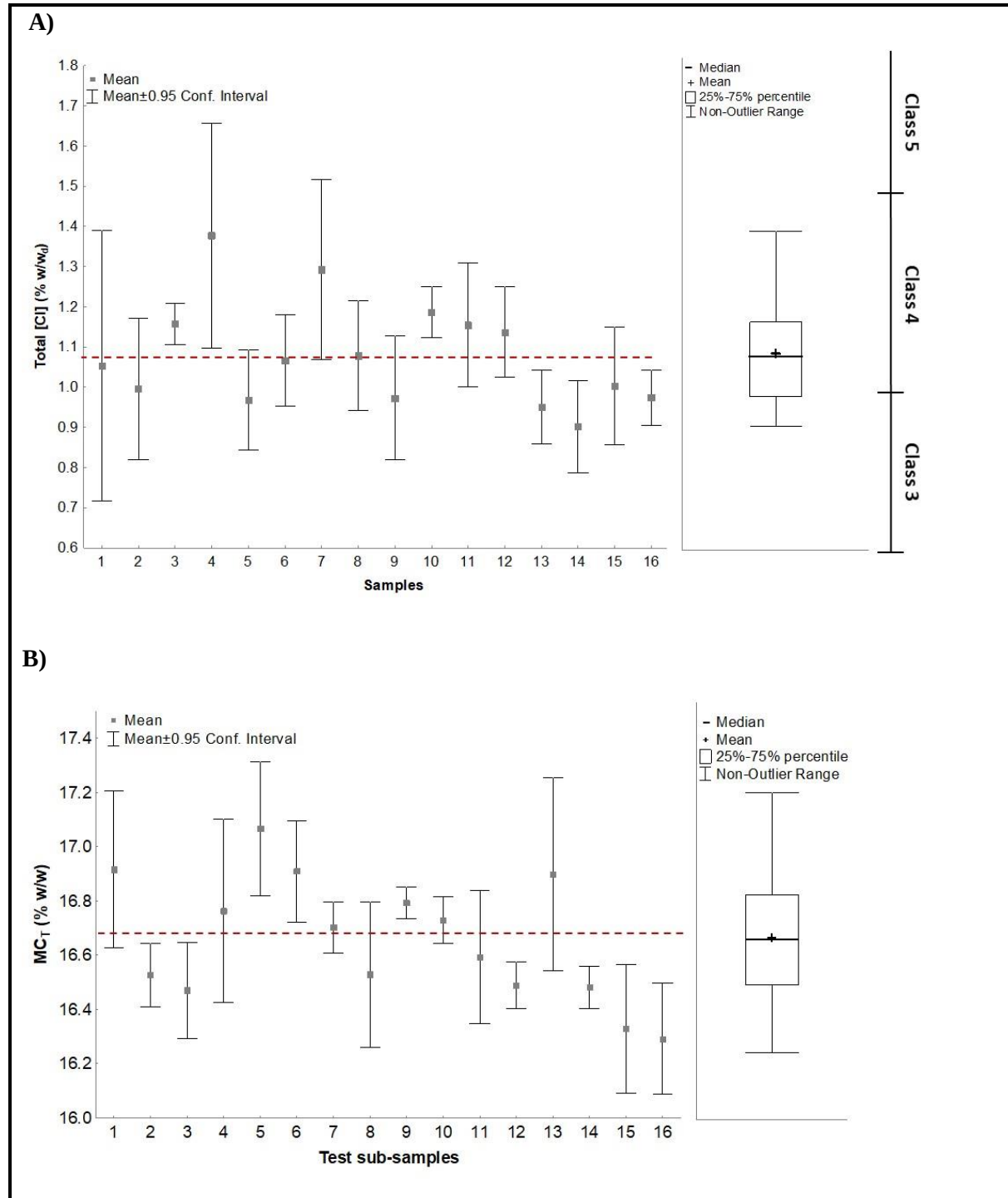


Figure 5-12. Variability of (A) Total [Cl] and (B) total MC (MC_T) in SRF sample delivered to the laboratory for analysis as calculated by the obtainment of 16 test sub-samples through the selected sub-sampling protocol. Class codes for the limit values of Cl content in SRF specified by CEN/TC 343 classification scheme (BS EN 15359, 2011).

In the case of MC, test sub-samples are more representative (**Figure 5-12**). For example, the 5th sub-sample with the highest MC (17.1% w/w) would overestimate the MC in the sample by 2.5%, whereas the 16th sub-sample with the lowest MC (16.3% w/w) would underestimate the MC by 2.2%. The difference between these values leads to a range of 0.8% w/w, which is equal with a relative range of 4.6%.

Table 5-10. Mean values of Total [Cl] in the 16 sub-samples (test sub-samples) and percentage difference of each sub-sample from the mean value of Total [Cl] in the samples (1.08%w/w_d).

Sub-samples	Total [Cl] (% w/w _d)	Uncertainty (%) in the mean value of Total [Cl]: 1.08% w/w _d
1	1.05	-2.8
2	1.00	-7.4
3	1.16	7.4
4	1.38	27.8
5	0.97	-10.2
6	1.07	-0.9
7	1.29	19.4
8	1.08	0.0
9	0.97	-10.2
10	1.19	10.2
11	1.16	7.4
12	1.14	5.6
13	0.95	-12.0
14	0.90	-16.7
15	1.00	-7.4
16	0.97	-10.2

Table 5-11 shows the interval estimations for binomial proportion through three different methods (normal approximation, exact Clopper-Pearson and Wilson score method – see **Appendix C1**) indicating the possibility to obtain representative test sub-samples ($\leq 15\%$) for determination of Total [Cl] in SRF. Based on Wilson score method – the most conservative estimation – the total number of representative SRF test sub-sample lies between 57 to 93% of total population with 95% confidence following the current sub-sampling plan (**Table 5-11**).

Table 5-11. Three different methods for the calculation of confidence intervals for binomial proportions indicating the possibility to obtain representative analytical results for the determination of Total [Cl] in SRF following the established sub-sampling plan to draw one test sub-sample – assuming that a test sub-sample that differs from the actual Total [Cl] in the initially obtained SRF sample (arithmetic mean of 16 sub-samples) less than 15% is representative – following the current sub-sampling plan.

Confidence interval for binomial proportions	Lower 95%	Upper 95%
Normal approximation method	0.62	1.00
Exact Clopper-Pearson method	0.54	0.96
Wilson score method	0.57	0.93

However, this possibility can be considerably reduced if we obtain and analyse two test sub-samples instead. By taking the pairwise average from two test sub-samples, only 5 pairs out of 120 were non-representative (> 15%) for the determination of Total [Cl] (**Table 5-12**).

Table 5-12. Average Total [Cl] for all possible combinations between two test sub-samples (pairwise averages) and percentage difference from actual Total [Cl] in the sample (1.08% w/w_d): averages of Total [Cl] between two sub-samples higher than 1.24 w/w_d and lower than 0.92 w/w_d differ from Total [Cl] in the sample more than 15%.

Average between two sub-samples																
Sub-samples	Total [Cl] (% w/w _d)	1 st with each sub-sample	2 nd with each sub-sample	3 rd with each sub-sample	4 th with each sub-sample	5 th with each sub-sample	6 th with each sub-sample	7 th with each sub-sample	8 th with each sub-sample	9 th with each sub-sample	10 th with each sub-sample	11 th with each sub-sample	12 th with each sub-sample	13 th with each sub-sample	14 th with each sub-sample	15 th with each sub-sample
1	1.05															
2	1.00	1.02														
3	1.16	1.11	1.08													
4	1.38	1.22	1.19	1.27												
5	0.97	1.01	0.98	1.06	1.17											
6	1.07	1.06	1.03	1.11	1.22	1.02										
7	1.29	1.17	1.14	1.23	1.34	1.13	1.18									
8	1.08	1.07	1.04	1.12	1.23	1.02	1.07	1.19								
9	0.97	1.01	0.98	1.07	1.18	0.97	1.02	1.13	1.03							
10	1.19	1.12	1.09	1.17	1.28	1.08	1.13	1.24	1.13	1.08						
11	1.16	1.10	1.08	1.16	1.27	1.06	1.11	1.22	1.12	1.06	1.17					
12	1.14	1.10	1.07	1.15	1.26	1.05	1.10	1.22	1.11	1.06	1.16	1.15				
13	0.95	1.00	0.97	1.05	1.16	0.96	1.01	1.12	1.01	0.96	1.07	1.05	1.04			
14	0.90	0.98	0.95	1.03	1.14	0.94	0.98	1.10	0.99	0.94	1.04	1.03	1.02	0.93		
15	1.00	1.03	1.00	1.08	1.19	0.99	1.04	1.15	1.04	0.99	1.10	1.08	1.07	0.98	0.95	
16	0.97	1.01	0.98	1.07	1.18	0.97	1.02	1.13	1.03	0.97	1.08	1.06	1.06	0.96	0.94	0.99
Lower difference from real Total [Cl] (%)	-12.57	-9.94	-17.39	-23.69	-4.74	-9.30	-14.86	-4.90	-0.04	-8.48	-6.20	0.83	9.52	11.73	8.42	
Upper difference from real Total [Cl] (%)	9.43	12.06	4.61	-5.59	13.36	8.80	-1.69	8.27	13.13	3.24	4.70	5.51	14.21	13.11	8.42	

Table 5-13 shows the possibility to obtain representative results for the determination of Total [Cl] in SRF by analyzing two test sub-samples instead of one. Based on Wilson score method, the total number of representative pairs of test sub-samples lies between 91 to 98% of total population with 95% confidence (**Table 5-13**).

Table 5-13. Three different methods for the calculation of confidence intervals for binomial proportions indicating the possibility to obtain representative results for the determination of Total [Cl] in SRF following the established sub-sampling plan to draw two test sub-samples instead of one – assuming that a test sub-sample that differs from the actual Total [Cl] in the initially obtained SRF sample (arithmetic mean of 16 sub-samples) less than 15% is representative.

Confidence interval for binomial proportions	Lower 95%	Upper 95%
Normal approximation method	0.92	0.99
Exact Clopper-Pearson method	0.91	0.99
Wilson score method	0.91	0.98

5.5 Statistical quantification of sub-sampling uncertainty: moisture, ash, NCV, and Cl

At this section the results obtained from the statistical quantification of uncertainty arising from sub-sampling for determination of classification SRF properties such as moisture, ash, Cl and calorific content by implementing DoE1 (**Section 4.2**) is presented, addressing the research objective (**O3**).

5.5.1 Descriptive statistics: Classification of SRF sample

Descriptive statistics that summarizes the analytical results of SRF properties were obtained (**Table 5-14**). Total [Cl] lies within a range of 1.02-1.18% w/w_d with 95% confidence, which designates the commercially produced sample as class code 4 for Total [Cl] (1 – 1.5% w/w_d). The NCV lies within 19.79 and 20.32 MJ kg⁻¹ with 95% confidence interval. This range contains the borderline between class code 3 (≥ 15 MJ kg⁻¹) and class code 2 (≥ 20 MJ kg⁻¹), but the average value (20.05 MJ kg⁻¹) designates the SRF sample as class code 2 for NCV. Based on the classification scheme for the quality of WDF, MC (economic quality parameter) specifies the sample as class code 3 ($\leq 20\%$ w/w), whereas Ash (technical quality parameter) defines the sample as class code 2 ($\leq 20\%$ w/w_d) (WRAP, 2012).

Table 5-14. Central tendency, spread and confidence intervals of SRF properties derived from 17 sub-samples of 53 g obtained from the balance nested designs through the established sub-sampling process.

Descriptive statistics*	$\bar{x}$	M	s.d.	95% CI	Range
MC (% w/w)	16.62	16.59	0.26	(16.48, 16.76)	[16.05, 17.07]
Ash (% w/w _d)	13.45	13.54	0.39	(13.26, 13.65)	[12.81, 14.19]
Total [Cl] (% w/w _d)**	1.09	1.07	0.15	(1.02, 1.18)	[0.90, 1.40]
NCV (MJ kg ⁻¹)	24.05	24.03	0.65	(23.72, 24.38)	[22.59, 25.22]
NCV (MJ kg ⁻¹)***	20.05	20.08	0.51	(19.79, 20.32)	[18.90, 21.00]

*Descriptive statistics derived from 17 SRF sub-samples including: arithmetic mean, median, standard deviation, 95% confidence interval and range between minimum and maximum values, respectively; ** Descriptive statistics only for Total [Cl] were calculated after the removal of systematic analytical error (1.7%); ***NCV expressed on wet basis (MJ kg⁻¹) in order to compare the values with the classification system (BS EN 15359, 2011)

5.5.2 Overall sub-sampling uncertainty: Nested design vs ToS

The key assumptions to use nested-ANOVA were checked for all critical SRF properties (see

Appendix D3) indicating that I can validly draw inferences about the results. **Table 5-15** presents the results of variance components obtained by nested-ANOVA indicating the variance arising from each stage of sub-sampling. In **Table 5-15**, the stage AE represents the variance of replicate measurements.

Table 5-15. Variance components obtained from nested-ANOVA indicating the variance of key SRF properties at each stage of sub-sampling process. Datasets used for conducting four level (*Gross_nested*) and three level (*Intra_nested*) nested-ANOVA derived from analytical results presented in **Appendix D2**.

Sub-sampling stages	d.f ¹	Variance components ²				Arithmetic mean ⁴			
		MC (% w/w)	Ash (% w/w _d)	Total [Cl] (% w/w _d)	NCV (MJ kg ⁻¹)	MC (% w/w)	Ash (% w/w _d)	Total [Cl] (% w/w _d)	NCV (MJ kg ⁻¹)
<i>Gross_nested</i>	1 st	1	0.008	0.045	0.001				
	2 nd	2	0.000	0.000	0.001				
	3 rd	4	0.028	0.061	0.007	16.66	13.47	1.08	24.06
	4 th	8	0.028	0.077	0.008				
	AE ³	32	0.007	0.042	0.004				
<i>Intra_nested</i>	5 th	1	0.047	0.029	0.004				
	6 th	2	0.028	0.164	0.010				
	7 th	4	0.013	0.182	0.012	16.05	13.23	1.39	23.92
	AE ³	16	0.016	0.054	0.003				

Sub-sampling stages	d.f. ¹	Variance components ²				Arithmetic mean ⁴			
		MC	Ash	Total [Cl]	NCV	MC	Ash	Total	NCV
		(% w/w)	(% w/w _d)	(% w/w _d)	(MJ kg _d ⁻¹)	(% w/w)	(% w/w _d)	[Cl] (% w/w _d)	(MJ kg _d ⁻¹)

¹Degrees of freedom for each level of nested ANOVA (Montgomery, 2017); ²Varriance of SRF properties between sub-samples nested within samples at each stage of sub-sampling; ³Variance of replicates (from test sub-sample to test portion) for both designs; ⁴Arithmetic mean of SRF properties for *Gross_nested* and *Intra_nested* that derived from 16 sub-samples and 8 sub-samples, respectively.

Along with the empirical calculation by nested-ANOVA (Table 5-15), ToS-formula was used to theoretically calculate the FE (see Appendix D4). Figure 5-13 presents the overall sub-sampling uncertainty (RSD) for key SRF properties as statistically calculated (nested design) and theoretically estimated (ToS). The uncertainty for NCV was calculated based only on nested design since ToS considers that analytes are contaminants, as mentioned in Section 4.2.8.2.

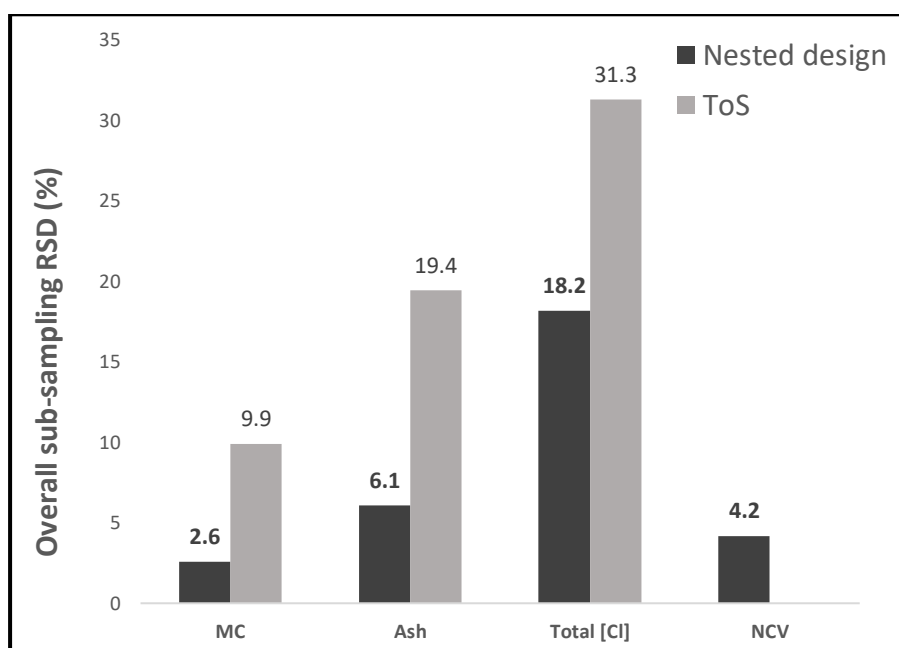


Figure 5-13. Overall uncertainty, expressed as RSD (%), arising from the established sub-sampling plan for the determination of SRF properties statistically (nested design) and theoretically (ToS) determined: NCV was calculated only statistically due to the consideration of ToS that analytes are contaminants.

5.5.3 Uncertainty arising from sub-sampling stages

5.5.3.1 Statistical significance: Representative sub-samples?

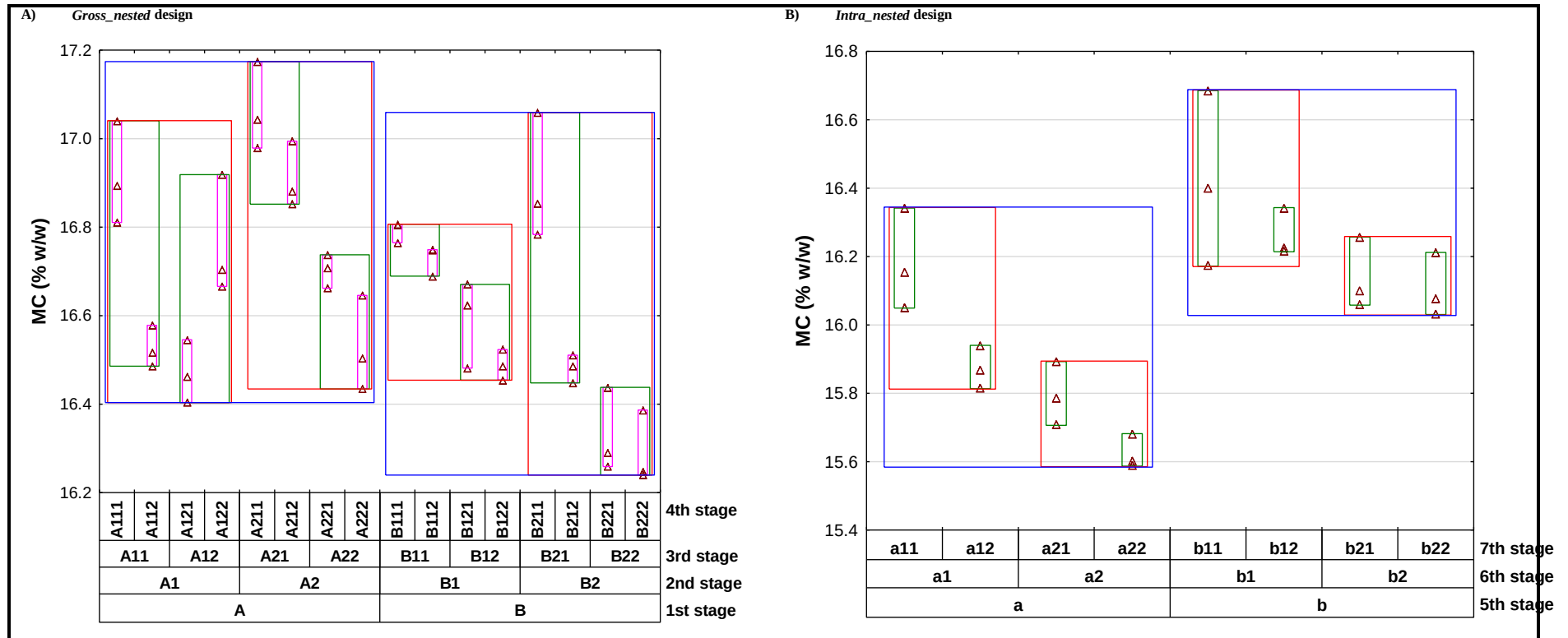
Table 5-16 presents the significance results of nested-ANOVA test for the stages of sub-sampling process. Test of significance is an evidence for the ability of a sub-sample to represent the higher level of sub-sample. Only in the final stages of *Gross_nested* and *Intra_nested* designs, the 4th and the 7th, respectively, there is significant difference between the sub-samples nested within samples at a significance level $\alpha = 0.05$. In the first stages, the null hypothesis cannot be rejected at a confidence interval 95%.

Table 5-16. Tests of Significance of nested-ANOVA for *Gross_nested* and *Intra_nested* designs at a significance level $\alpha=0.05$ for SRF quality determination.

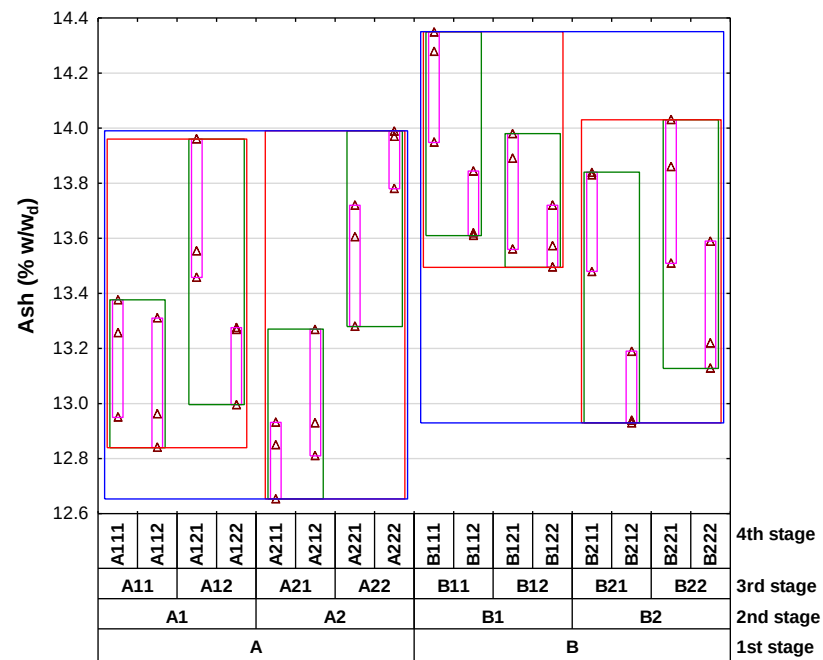
Nested design	Sub-sampling	Null hypothesis ¹	d.f.	MC (% w/w)	Ash (% w/w _d)	CI (% w/w _d)	NCV (MJ kg _d ⁻¹)
Gross	1 st stage	$\bar{X}_A = \bar{X}_B$	1	ND	ND	ND	ND
	2 nd stage	$\bar{X}_{A1} = \bar{X}_{A2}$ AND $\bar{X}_{B1} = \bar{X}_{B2}$	2	ND	ND	ND	ND
	3 rd stage	$\bar{X}_{A11} = \bar{X}_{A12}$ AND $\bar{X}_{A21} = \bar{X}_{A22}$ AND $\bar{X}_{B11} = \bar{X}_{B12}$ AND $\bar{X}_{B21} = \bar{X}_{B22}$	4	ND	ND	ND	ND
	4 th stage	$\bar{X}_{A111} = \bar{X}_{A112}$ AND $\bar{X}_{A121} = \bar{X}_{A122}$ AND $\bar{X}_{A211} = \bar{X}_{A212}$ AND $\bar{X}_{A221} = \bar{X}_{A222}$ AND $\bar{X}_{B111} = \bar{X}_{B112}$ AND $\bar{X}_{B121} = \bar{X}_{B122}$ AND $\bar{X}_{B211} = \bar{X}_{B212}$ AND $\bar{X}_{B221} = \bar{X}_{B222}$	8	SD	SD	SD	SD
Intra	5 th stage	$\bar{X}_a = \bar{X}_b$	1	ND	ND	ND	ND
	6 th stage	$\bar{X}_{a1} = \bar{X}_{a2}$ AND $\bar{X}_{b1} = \bar{X}_{b2}$	2	ND	ND	ND	ND
	7 th stage	$\bar{X}_{a11} = \bar{X}_{a12}$ AND $\bar{X}_{a21} = \bar{X}_{a22}$ AND $\bar{X}_{b11} = \bar{X}_{b12}$ AND $\bar{X}_{b21} = \bar{X}_{b22}$	4	SD	SD	SD	SD

¹Null hypothesis at each level of nested ANOVA based on the balanced nested designs (*Gross_nested* and *Intra_nested*), $\bar{X}$ represents the arithmetic mean of the selected SRF property in the related sub-samples of each stage; SD: statistical difference; ND: No statistical difference

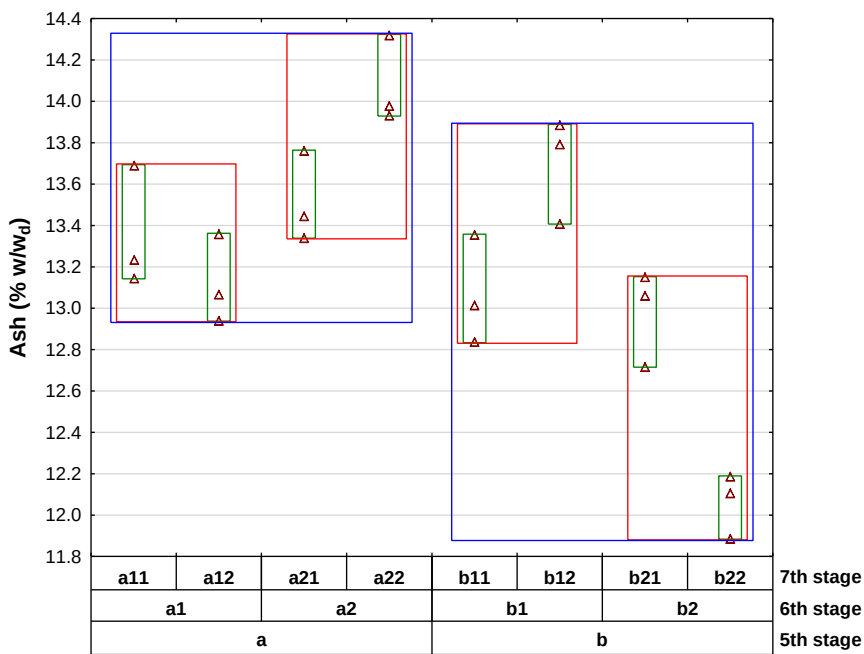
In order to get better insights into the difference between sub-samples, variability plots demonstrating the spread of analytical values between nested sub-samples were obtained (**Figure 5-14**). The blue parallelograms represent the sub-samples of the first stage of riffle splitting for both designs, the red parallelograms nested within the blue ones indicate the sub-samples of the second stage, etc. In most pairs of nested sub-samples, the spread of values looks quite alike. In the 2nd stage, the sub-samples (red parallelograms of *Gross_nested* design) look more uniform pairwise compared to the other stages due to shredding with the cutting mill applied before the 2nd stage. In the 7th stage, the nested sub-samples present a higher spread of values (green parallelograms of *Intra_nested* design) due to their low mass.

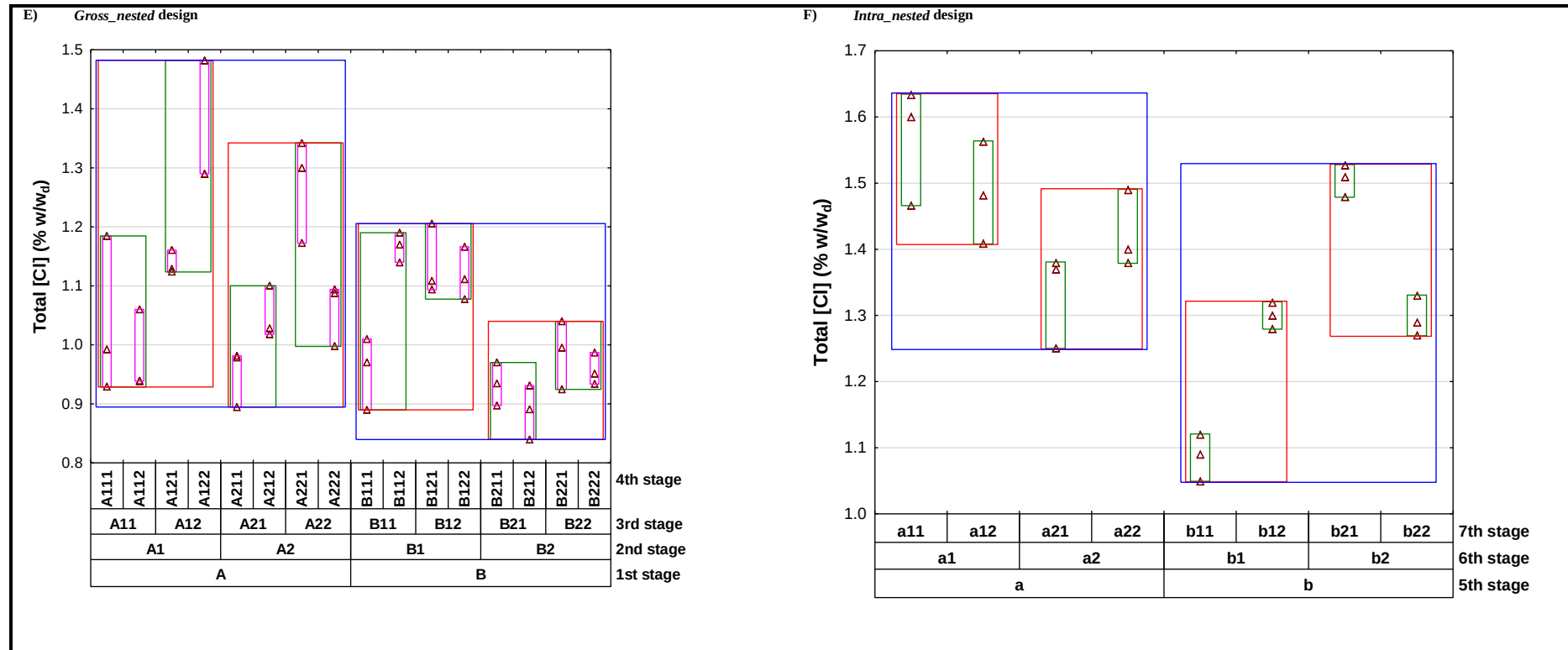


C) *Gross_nested design*



D) *Intra_nested design*





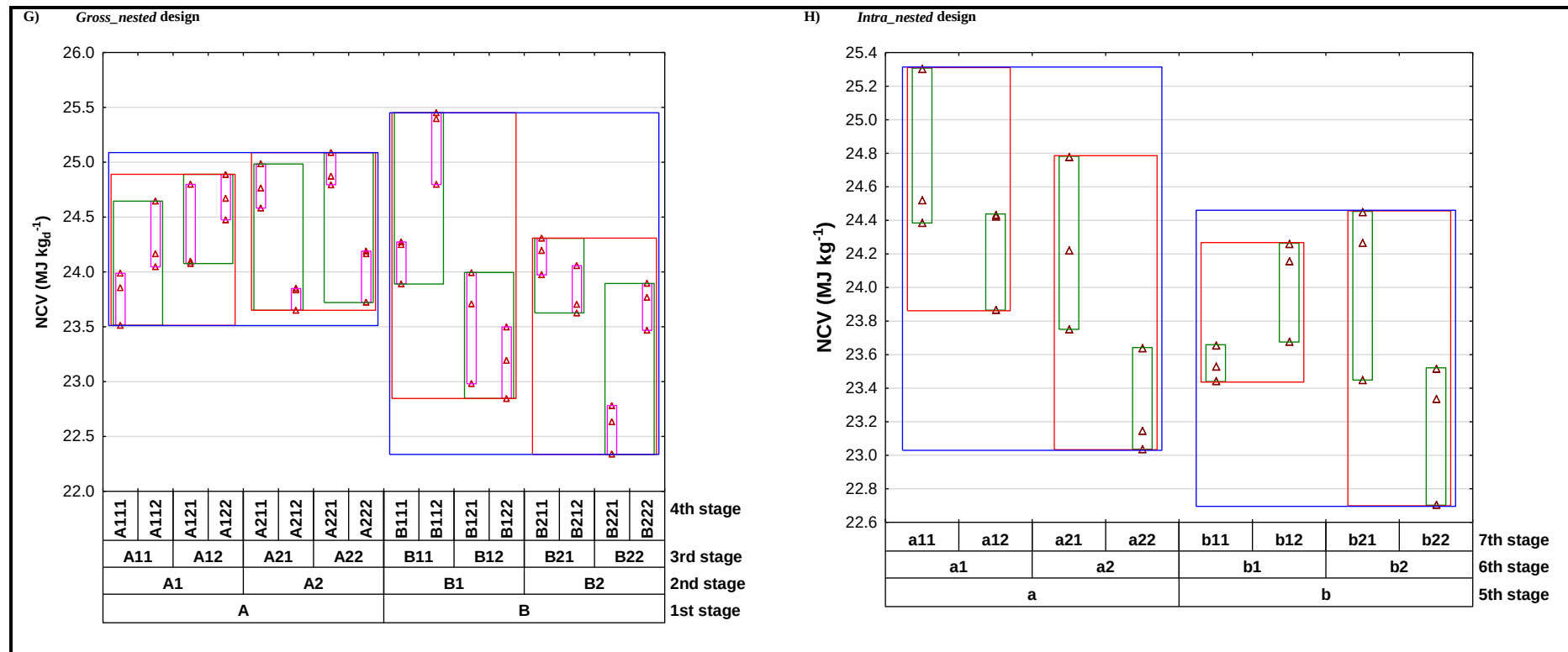


Figure 5-14. Variability plots of SRF properties between sub-samples nested within sample at each stage of sub-sampling process. **A:** Variability plot of MC from the 1st to the 4th sampling stage (*Gross_nested*); **B:** Variability plot of MC from the 5th to the 7th sampling stage (*Intra_nested*); **C:** Variability plot of Ash from the 1st to the 4th sampling stage (*Gross_nested*); **D:** Variability plot of Ash from the 5th to the 7th sampling stage (*Intra_nested*); **E:** Variability plot of Total [Cl] from the 1st to the 4th sampling stage (*Gross_nested*); **F:** Variability plot of Total [Cl] from the 5th to the 7th sampling stage (*Intra_nested*); **G:** Variability plot of NCV from the 1st to the 4th sampling stage (*Gross_nested*); **H:** Variability plot of NCV from the 5th to the 7th sampling stage (*Intra_nested*). The blue rectangles represent the first stage of riffle splitting for both nested designs (1st sub-sampling stage for *Gross_nested* and 5th sub-sampling stage for *Intra_nested*); the red rectangles represent the second stage of riffle splitting (2nd sub-sampling stage for *Gross_nested* and 6th sub-sampling stage for *Intra_nested*); the green rectangles represent the third stage of riffle splitting (3rd sub-sampling stage for *Gross_nested* and 7th sub-sampling stage for *Intra_nested*); the pink rectangles represent the fourth stage of riffle splitting (4th sub-sampling stage for *Gross_nested*); triangles represent the individual measurements taken for both designs (see analytical results in **Appendix D2**).

5.5.3.2 Sub-sampling uncertainty at each stage: Nested design vs ToS

The variance components (**Table 5-15**) provided by nested-ANOVA used for the calculation of RSD arising from each sub-sampling stage are shown in Error! Reference source not found. **Table 5-17**. For all fuel properties, the RSD presents an upward trend as the sub-sampling process unfolds. However, the RSD arising from the 2nd stage of sub-sampling is zero for all properties except for Total [Cl] that remains almost constant (2.2%). Likewise, the RSD arising from the 4th stage is higher than the 5th stage for most SRF properties (except to MC).

Table 5-17. Sub-sampling uncertainty, expressed as RSD (%), arising from each stage of the established sub-sampling plan for the determination of key SRF properties statistically calculated (nested design).

Sub-sampling stages		RSD (%) [*]			
		MC	Ash	Total [Cl]	NCV
1 st	From 850 g to 425 g	0.5	1.6	2.3	1.4
2 nd	From 425 g to 212 g	0.0	0.0	2.2	0.0
3 rd	From 212 g to 106 g	1.0	1.8	7.8	1.8
4 th	From 160 g to 53 g	1.0	2.1	8.5	2.2
5 th	From 53 g to 26 g	1.4	1.3	4.5	0.6
6 th	From 26 g to 13 g	1.0	3.1	7.2	0.2
7 th	From 13 g to 6.5 g	0.7	3.2	7.9	2.0
AE ^{**}	From 6.5 g to test portion	0.7	1.6	5.0	1.4

^{*} Relative standard deviation derived from the ratio of variance components at each sub-sampling stage given by nested-ANOVA to the arithmetic mean of SRF properties in 16 test sub-samples for *Gross_nested* and 8 test sub-samples for *Intra_nested* design; ^{**} RSD of AE stage derives from the variance of replicates including the analytical error and the sub-sampling uncertainty arising from test sub-sample to test portion

The statistically calculated RSD (nested design) was compared with the theoretically estimated RSD (ToS) arising from each sub-sampling stage (**Figure 5-15**). ToS provides considerably higher RSD compared to nested design in stages that shredding was not applied: in the 1st stage for all SRF properties (mass reduction with initial $d \approx 3$ cm); and in the AE stage for MC and Ash (collection of test portions without cryogenic shredding). In the intermediate stages, from the 2nd to the 6th, the results between nested design and ToS seem more compatible. The difference of RSD between the 1st and 2nd stage is higher in the theoretical approach rather than the statistical approach. For example, the

RSD arising from the 1st stage is at least 10 times higher than the 2nd stage of sub-sampling for the determination of Total [Cl] based on ToS, while nested design demonstrates that the RSD arising from the 1st (2.3%) and 2nd stage (2.2%) are similar.

The relative contribution of each stage of sub-sampling to the overall RSD based on both approaches is presented (**Figure 5-16**). According to ToS, for the determination of Total [Cl] the relative contribution of the sub-sampling stages to the overall uncertainty is formed in an order 1st > 7th > 6th > 5th > 4th > 3rd > 2nd > AE. For MC and Ash the order is slightly different due to absence of shredding the test sub-samples with CryoMill increasing the uncertainty emerging from the final AE stage: AE > 1st > 7th > 6th > 5th > 4th > 3rd > 2nd.

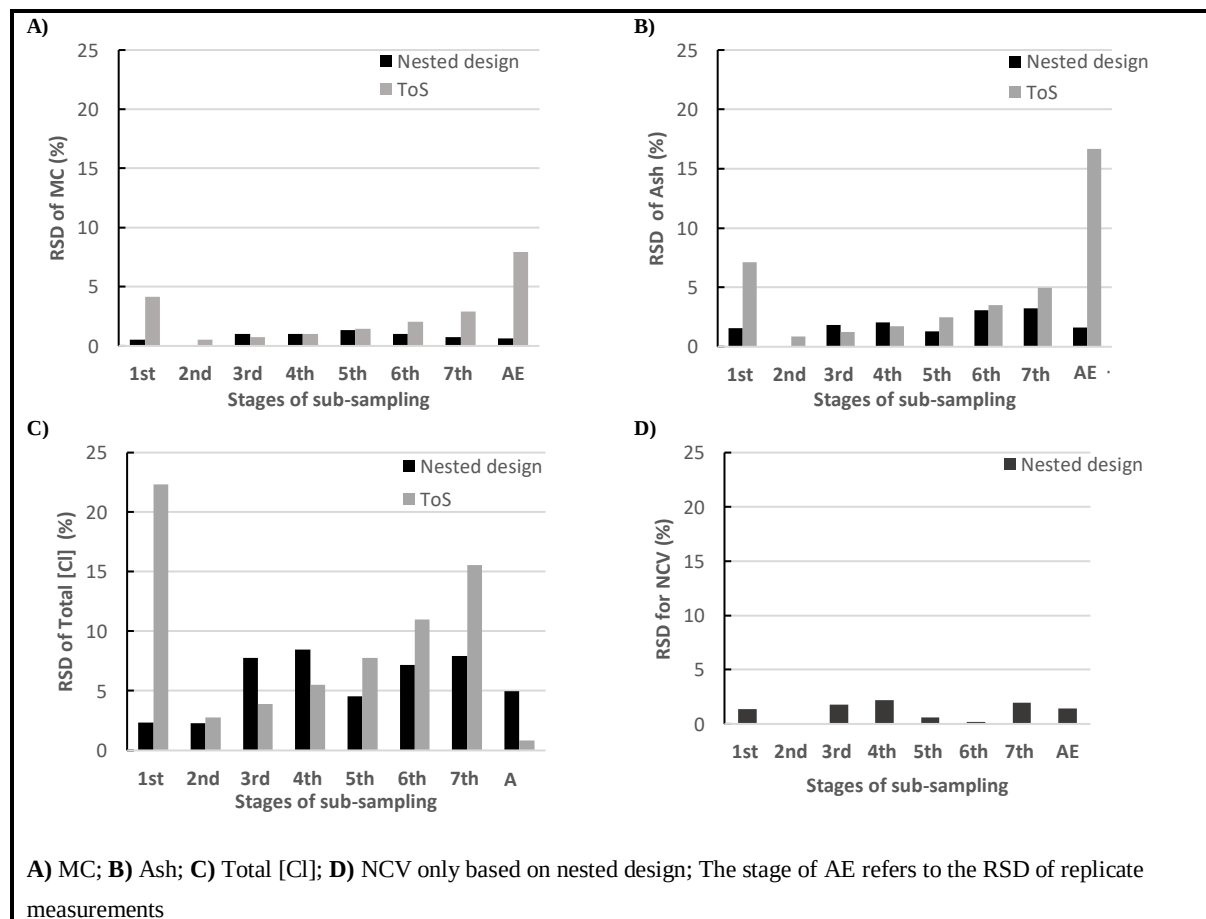


Figure 5-15. Sub-sampling uncertainty, expressed as RSD (%), arising from each sub-sampling stage for the determination of key SRF properties calculated statistically (nested design) and theoretically (ToS): NCV was calculated only statistically due to the consideration of ToS that analytes are contaminants.

According to nested design, the relative contribution of each stage to the overall RSD is different for each SRF property. For example, in case of MC the order is 5th > 6th > 3rd > 4th > 7th > AE > 1st > 2nd,

for Ash is $7^{\text{th}} > 6^{\text{th}} > 4^{\text{th}} > 3^{\text{rd}} > \text{AE} > 1^{\text{st}} > 5^{\text{th}} > 2^{\text{nd}}$, for Total [Cl] is $7^{\text{th}} > 6^{\text{th}} > 4^{\text{th}} > 3^{\text{rd}} > 5^{\text{th}} > \text{AE} > 1^{\text{st}} > 2^{\text{nd}}$ and for NCV is $4^{\text{th}} > 7^{\text{th}} > 3^{\text{rd}} > \text{AE} > 1^{\text{st}} > 5^{\text{th}} > 6^{\text{th}} > 5^{\text{th}} > 2^{\text{nd}}$. Based ToS, the order of the relative contribution of the sub-sampling stages to the overall uncertainty should be the same for all analytes under an identical sub-sampling plan, but nested design showed that the relative contribution depends on fuel property.

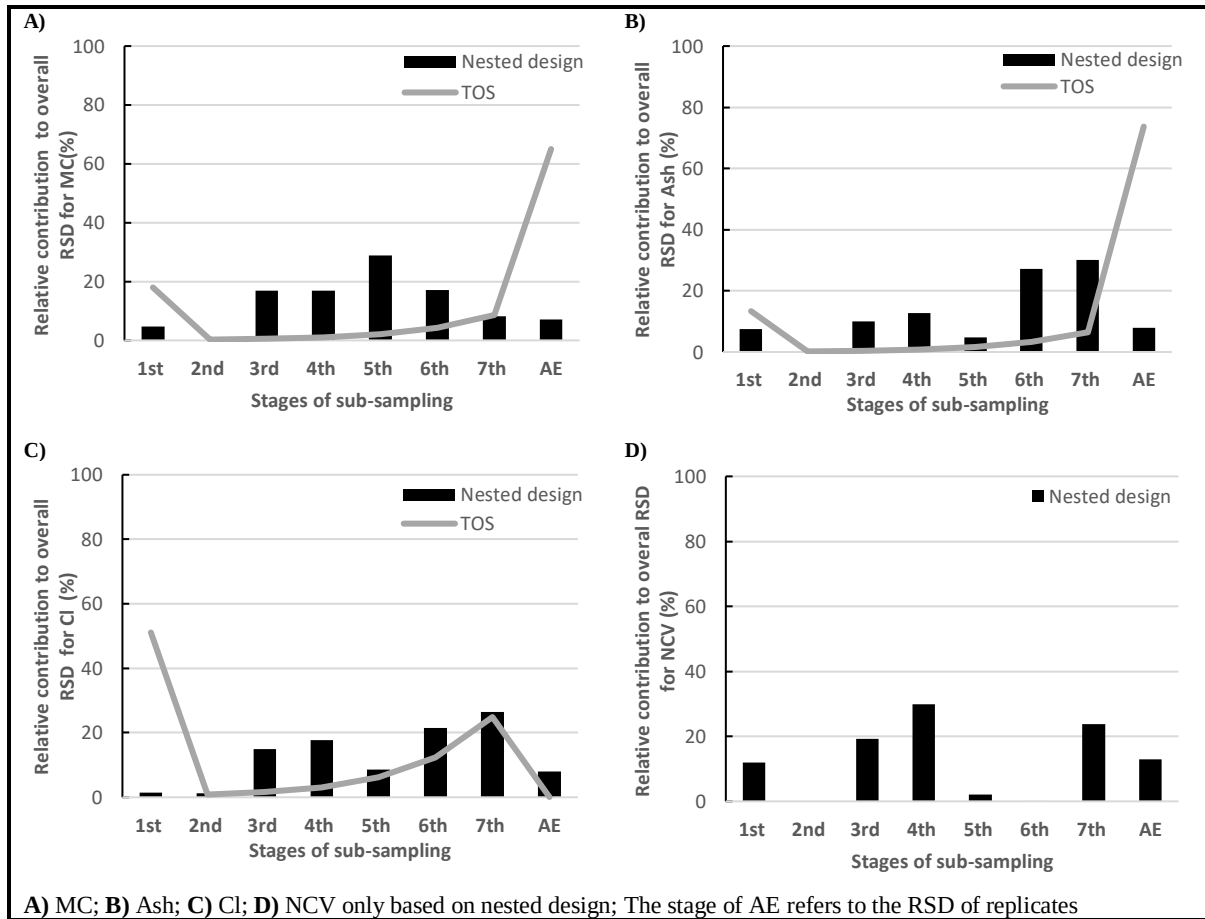


Figure 5-16. Relative contribution of sub-sampling stages to the overall sub-sampling uncertainty (RSD) for the determination of SRF properties based on the statistical (nested design) and theoretical approach (ToS): NCV was calculated only statistically due to the consideration of ToS that analytes are contaminants.

5.6 Statistical quantification of sub-sampling uncertainty for TG-DTG

At this section the results obtained from the statistical quantification of uncertainty arising from sub-sampling for determination of SRF combustion behaviour with the use of TG-DTG by implementing DoE1 (Section 4.2) is presented, addressing the research objective (O3).

5.6.1 Combustion behaviour of SRF

Figure 5-17 illustrates the TG-DTG profile of the SRF sample derived from averaging TG-DTG results of 17 sub-samples used for both nested designs. Under the selected TG-DTG operating conditions, SRF sample is decomposed in a temperature range of 238 – 664 °C, whereas the residue matter after combustion is 12.85% w/w. The first DTG peak is due to evaporation of residual moisture leading to a mass loss of 2.57% w/w. The next two peaks denote the mass loss of volatile lignocellulosic materials in SRF: the first DTG shoulder is mainly due to decomposition of hemicellulose – with maximum rate of mass loss 3.11% w/w min⁻¹ at 238.6 °C; and the second DTG peak is mainly due to cellulose decomposition – with maximum rate 6.22% w/w min⁻¹ at 297.36 °C. The mass loss induced by these DTG peaks were 7.6% w/w and 43.4% w/w, respectively. The third peak has the highest rate of mass loss (8.58% w/w min⁻¹ at 425.30 °C) attributed to degradation of plastic fraction in SRF inducing a mass loss nearly 30% w/w. The last weak peak observed in a high temperature range (599 – 664 °C) is due to interaction of char with oxygen and formation of mineral matter induced by ash deformation (Çepelioğullar et al., 2016). Similar combustion characteristics of SRF under identical heating rate (10 °C min⁻¹) were obtained from previous studies **Table 2-5**.

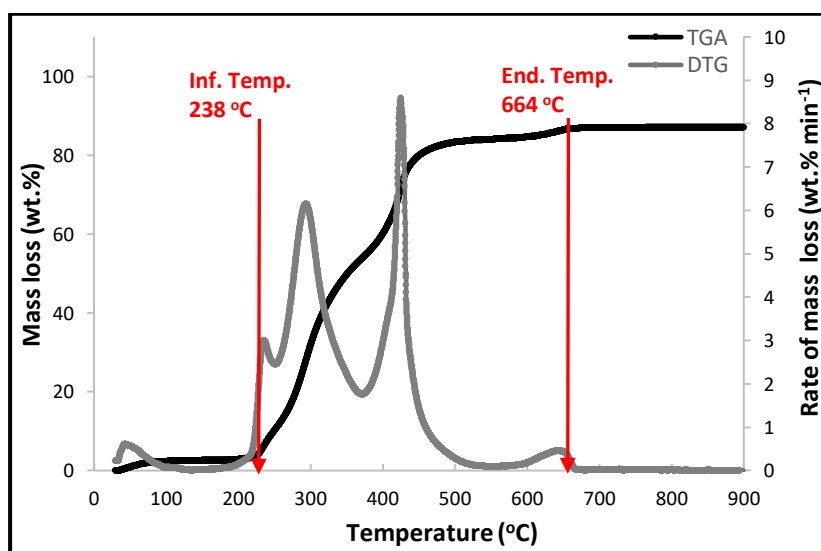


Figure 5-17. TG-DTG profile of SRF under non-isothermal operating conditions (atmosphere: air; flow rate: 50 ml min⁻¹; heating rate: 10 °C min⁻¹; sample holder: alumina 150 µl; sample mass: 10 mg; maximum temperature: 900 °C) obtained from the average of 17 sub-samples. Main features of the TG-DTG curve of SRF are: i) wide range of decomposition temperature (238 – 663 °C); ii) three main decomposition areas excluding moisture evaporation; and iii) maximum rate of mass loss at 3rd peak that corresponds to thermal decomposition of plastic fraction.

5.6.2 PCA for characteristic TG-DTG points

Before PCA to capture the thermal critical points with the highest variation, the presence of outliers was examined indicating no outliers for the present dataset (E1). **Figure 5-18** shows that four major PCs were retrieved capturing 65.73% of the total variation of the herein dataset. After the first four PCs, the loading values of these variables were less than 0.60 and therefore were not included in the analysis.

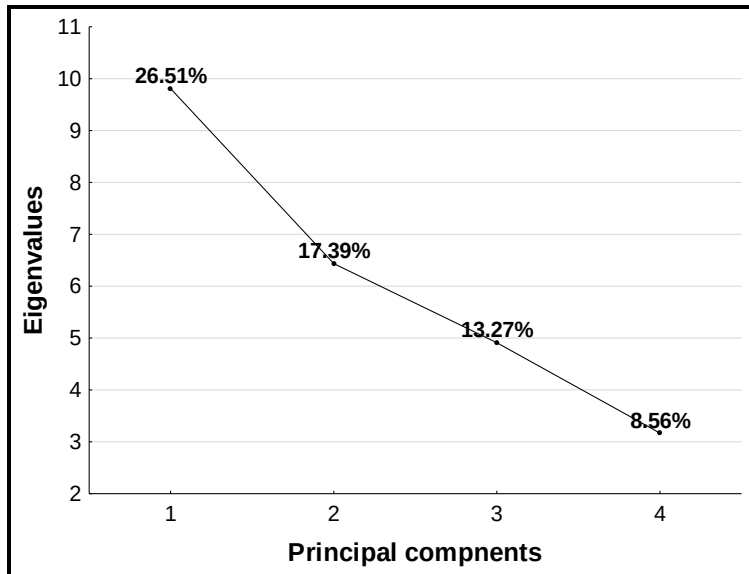


Figure 5-18. Scree plot of the eigenvalues of retaining principal components obtained by PCA indicating the amount of variation captured by each component from 37 characteristic points of TG-DTG curve of SRF expressed as a percentage: total captured variability equals to 65.73%.

Figure 5-19 shows the correlation of the variables referred to 37 TG-DTG points with the selected four PCs. The numbers of these variables indicate the corresponding thermal critical point from **Table 4-5**. The dotted grey square shows which variables were grouped by PCs: variables outside the square have high correlation with the corresponding PC (loading ≥ 0.60), whereas variables inside the square are not sufficiently correlated with PCs.

The first loading plot shows the correlation of the first two PCs (PC1 and PC2) with the 37 variables (**Figure 5-19**): variables with number 1, 2, 3, 5, 15, 16, 17, 24, 29, 32, and 33 derived from both TGA and DTG analysis are positively correlated with PC1 and variables with number 9 and 30 are negatively correlated with PC1. Similarly, variables with number 10, 12, 24, 25, and 26 have a negative correlation with PC2, whereas variable 4 has a positive correlation with PC2. This finding is

also confirmed by the second loading plot that shows the variables that are more influential in determining PC2 and PC3. Following this plot, variables 6, 18, 19, 20, 23, 34, and 36 have the greatest influence in PC3 with variable 23 having a positive correlation and the remaining variables having negative correlation with PC3. The third loading plot indicates that PC4 is considerably influenced only by variable 22 – negative correlation. The loading values of all variables for each PC can be found in **Appendix E2**.

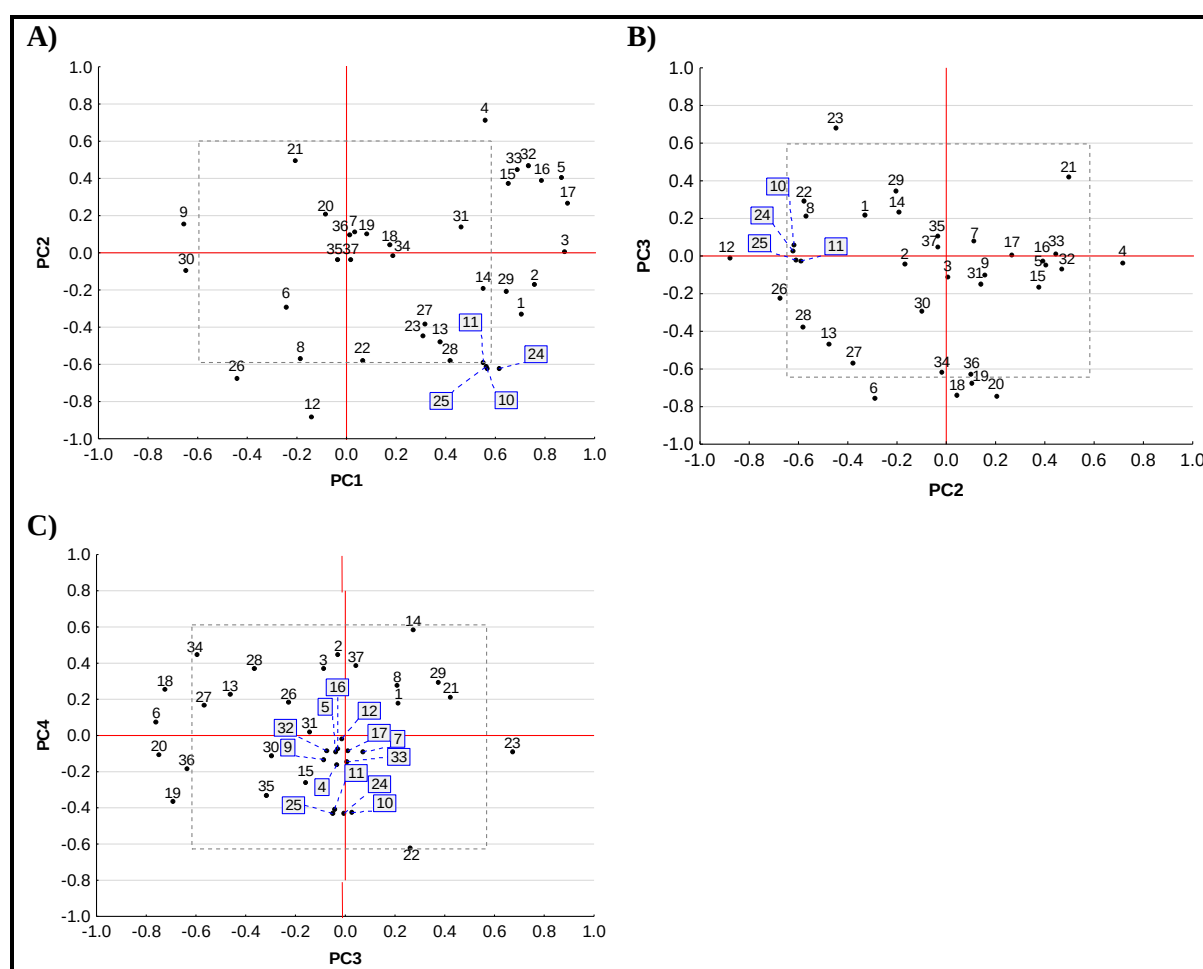
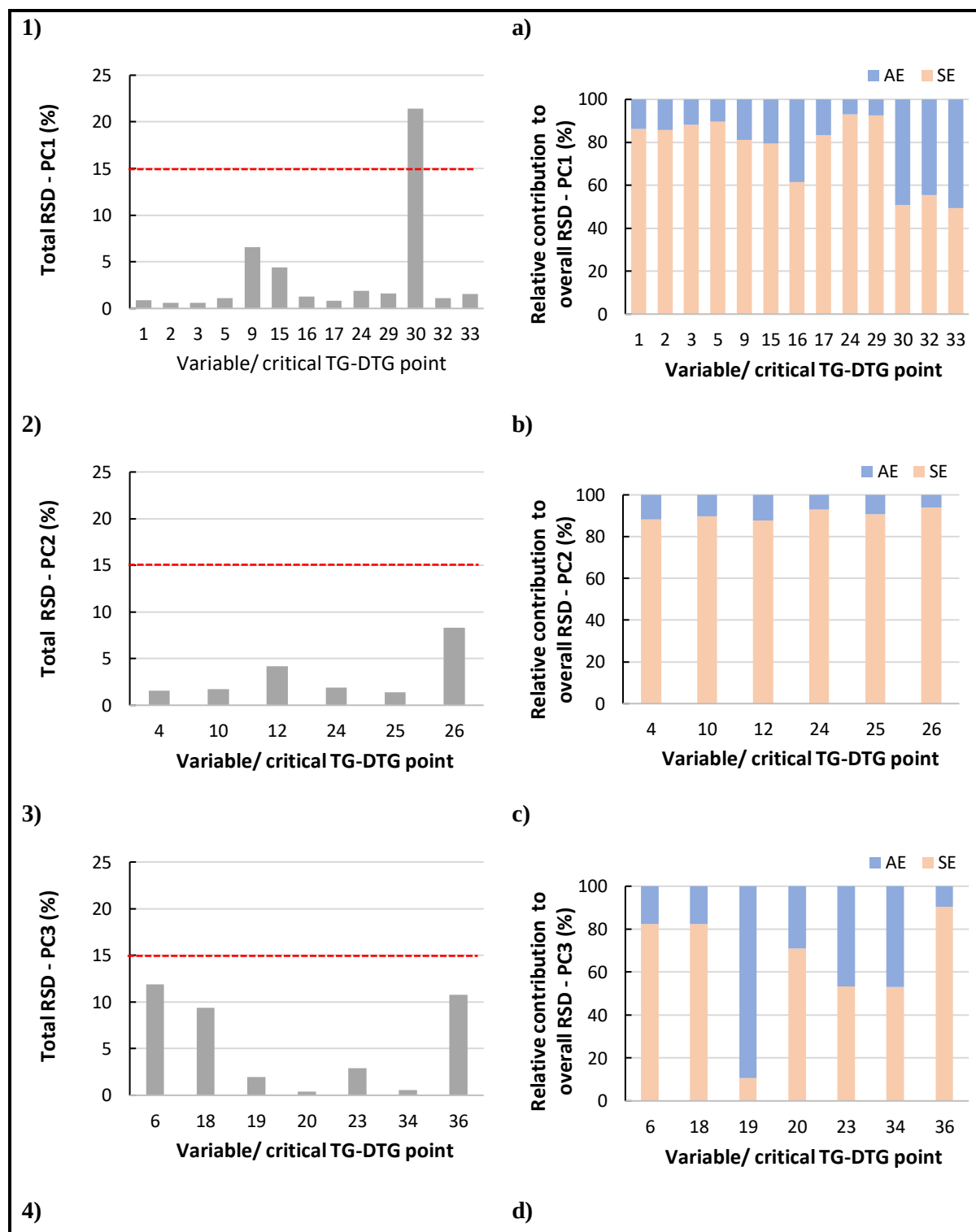


Figure 5-19. Loading scatterplot between the retaining PCs obtained by PCA after normalisation of raw data that contain characteristic points of TG-DTG curve of SRF derived from both Gross_nested and Intra_nested design: A) PC1 vs PC2; B) PC2 vs PC3; C) PC3 vs PC4. Variables (characteristic TG-DTG points) with loading values ≥ 0.60 (outside of the grey dotted square) were clustered in the corresponding PC: PC1 includes 12 variables with number 1, 2, 3, 5, 9, 15, 16, 17, 24, 29, 30, 32, and 33; PC2 includes 6 variables with number 4, 10, 12, 24, 25, and 26; PC3 includes 7 variables with number 6, 18, 19, 20, 23, 34, and 36; PC4 includes only one variable with number 22. Note: variable 24 (1st_Peak.T) is captured by both PC1 and PC2.

5.6.3 Sub-sampling uncertainty: nested-ANOVA

Key assumptions for the use of ANOVA test were mostly fulfilled for all variables including 37 critical TG-DTG points and combustibility index (S) in both balanced nested designs (**Appendix E3**).



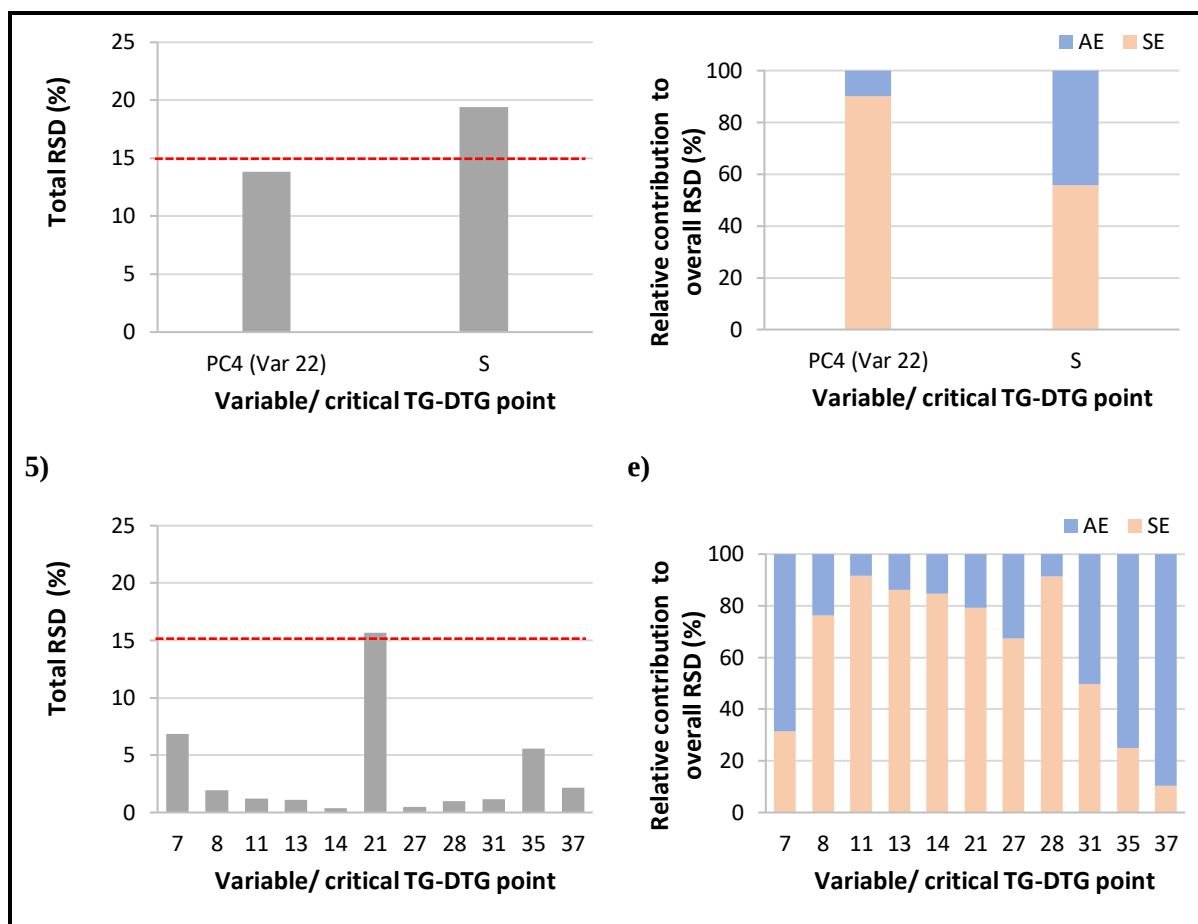


Figure 5-20. Total sub-sampling uncertainty, expressed as total RSD (%), for selected characteristic points of TG-DTG curve of SRF sample calculated by nested-ANOVA (1-5) and relative contribution of both error arising from all sub-sampling stages, defined as sub-sampling error (SE), and error arising from TG-DTG analysis, defined as analytical error (AE), to total RSD (a-e) as clustered by PCA: **1,a** include variables (characteristic TG-DTG points) captured by PC1; **2,b** include variables captured by PC2; **3,c** include variables captured by PC3; **4,d** include PC4 (only one variable is captured: Var 22) and S; **5,e** include all other characteristic TG-DTG points that were not captured by PCA. The red dotted line indicated the variables that exceeded the reference limit value (RSD > 15%).

Figure 5-20 illustrates the overall RSD arising from the established sub-sampling plan of SRF for several critical points of TG-DTG grouped by PCs along with the relative contribution of sub-sampling process (from initial sample to test sub-sample: SE) and analytical stage (from test sub-sample to test portion including analysis: AE) to total RSD. The relative contributions of SE and AE for variables grouped in PC1 have relatively similar levels for most of them, but the contribution of SE is lower and therefore the contribution of AE is higher for variables 16, 30, 32, and 33 (**Figure 5-20**). In addition, relative contributions are homogeneous for variables of PC2, whereas a wide dispersion is observed in PC3. Tables including variance of components from nested-ANOVA test,

RSD arising from each stage of riffle splitting along with total RSD, and relative contribution of SE and AE can be found in **Appendix E4**.

Figure 5-21 shows the variability plots of total RSD and relative contribution of SE and AE for the three PCs. Total RSD is quite similar for most of the variables (1, 2, 3, 5, 16, 17, 24, 29, 33) grouped in PC1, although variables 9, 15, and especially 30 give different values of total RSD. Similarly, in PC2, variables 4, 10, 24, and 25 have almost the same total RSD, whereas variable 12 and 26 differ from the others. For PC3, total RSD is similar for the variables 20 and 34, slightly higher for the variables 19 and 23, and considerably higher but still less than the acceptable limit for the variables 6, 18, and 36.

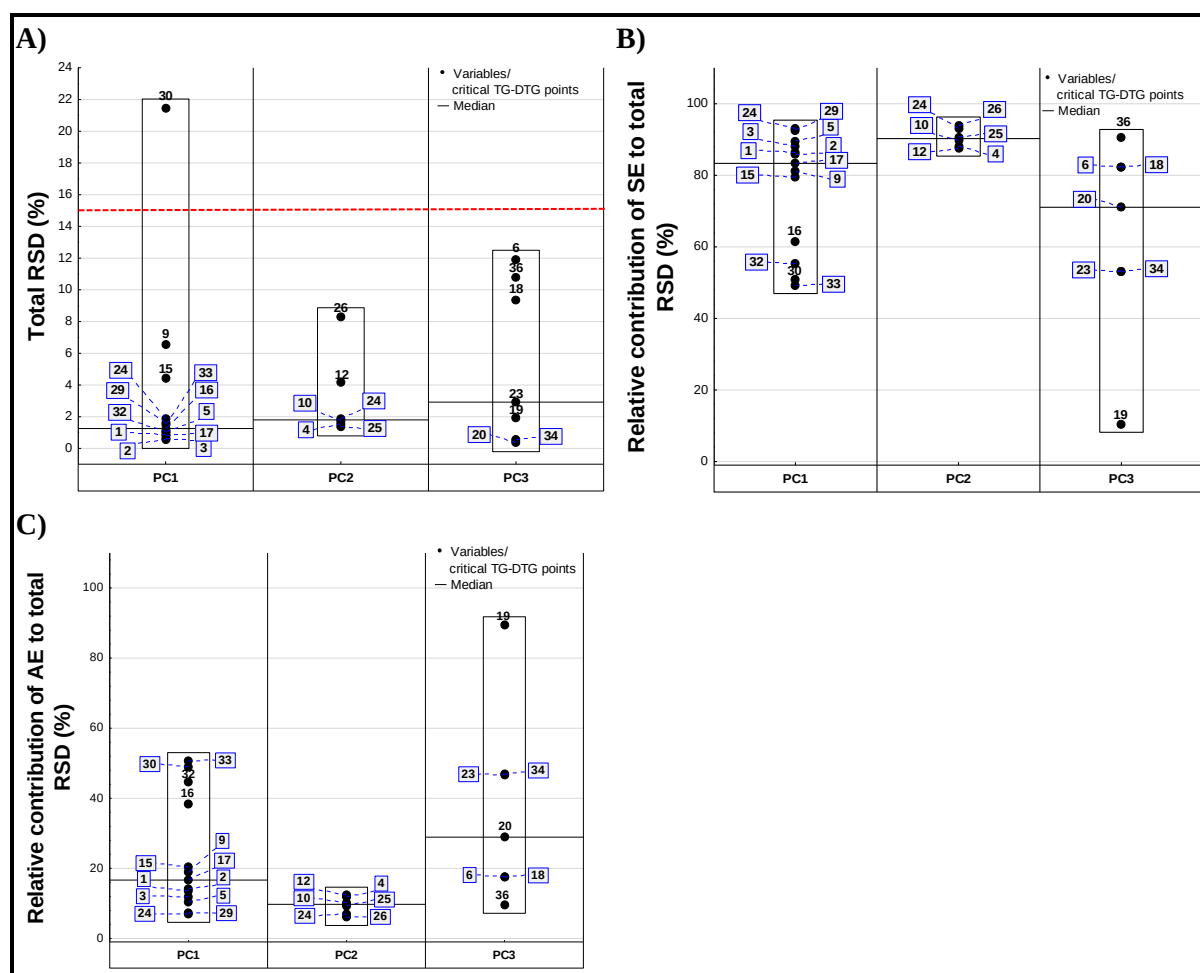


Figure 5-21. Variability plot obtained by grouping the characteristic TG-DTG points into PCs with PCA for: **A)** Total RSD: the red dotted line indicate the reference limit value (total RSD > 15%); **B)** Relative contribution of error arising from all sub-sampling stages, defined as sub-sampling error (SE), to total RSD; **C)** Relative contribution of error arising from TG-DTG analysis, defined as analytical error (AE), to total RSD. Only variable 30 (3rd_RML) exceeded the reference limit value, whereas SE is the prevalent source of total RSD for the majority of variables excluding variables 33 and 19 where the main source is AE.

The composite RSD and the respective relative contributions for PCs and total 38 TG-DTG points is shown in **Table 5-18**. The uncertainty for PC1 and PC3 is identical, although in PC1 the contribution of AE (28.1%) is lower compared to PC3 (48.1%). The lowest RSD is observed in PC2 (4%), whereas the highest is observed in the determination of PC4 (10.8%) which represents the 4th DTG peak. For the determination of other combustion characteristic points not captured by PCA the uncertainty is low (6.6%). The overall RSD for determination of total 38 critical points is 7% with AE and SE contributing to overall RSD by 35.9% and 64.1%, respectively. However, DTG critical points present a higher RSD (7.2%) compared to TGA points (5.5%) due to the high uncertainty to the 3rd DTG peak (variable 30), whereas the relative contributions of AE is slightly higher in DTG (40.8%) compared to TGA (30.2%) indicating the higher sensitivity analysis of DTG compared to TGA.

Table 5-18. Composite sub-sampling uncertainty (RSD_{pooled} : %) combined with relative contributions of both SE (error from all stages of riffle splitting and shredding) and AE (error from analysis and mass reduction from test sample to test portion) for each PC, all PCs, critical points not captured by PCA, DTG and TGD points separately, and the total 38 TG-DTG points indicating the sub-sampling uncertainty for determination of critical TG-DTG points for SRF combustion behaviour. Note: RSD did not exceed the reference limit value ($RSD \leq 15\%$).

Combustion characteristic points			
	Overall uncertainty	Relative contribution	
	RSD_{pooled} (%)	AE (%)	SE(%)
PC1*	6.4	28.1	71.9
PC2**	4.0	9.7	90.3
PC3***	6.4	48.1	51.9
PC4****	10.8	9.8	90.2
Total PCs ¹	6.3	28.6	71.4
Points not included in PCA	6.6	44.4	55.6
S	19.4	44.2	55.8
TGA points (1-21 variables)	5.5	30.2	69.8
DTG points (22-37 variables)	7.2	41.3	59.2
Combustion behaviour²	7.0	35.9	64.1

* PC1 includes 13 critical TG-DTG points: T10%, T20%, T30%, T75%, 1st_ML, 3rd_ML, 3rd_Inf.T, 3rd_Mid.T, 1st_Peak.T, 2nd_End.T, 3rd_RML, 3rd_Peak.T, 3rd_End.T; ** PC2 includes 6 critical TG-DTG points: T50%, 1st_Inf.T, 2nd_ML, 1st_End.T, 2nd_RML, 1st_Peak.T; *** PC3 includes 7 critical TG-DTG points: Res.MC, 4th_ML, 4th_Inf.T, 4th_Mid.T, 1st_On.T, 4th_RML, 4th_Peak.T; **** PC4 includes only 4th_Peak.T; ¹Derived from RSD_{pooled} of PCs;

²Derived from RSD_{pooled} of 38 critical points including S

Considering the relative contributions of SE and AE for TGA and DTG critical points from **Table 5-18**, the overall RSD for determination of entire TG-DTG signal was quantified as **Table 5-19**

presents. Uncertainty is higher for DTG (44%) than TGA (11.6%) which fluctuates at acceptable levels (<15%). By combining TGA with DTG, which are coupled techniques used concurrently in most of the times, the RSD becomes 32.2%.

Table 5-19. Sub-sampling uncertainty (RSD_{pooled}: %) for determination of entire TG-DTG signal of SRF.

RSD _{pooled} (%)	Entire TG-DTG signal		
	TGA	DTG	TG-DTG
AE ¹	6.4	28.3	20.5
SE ²	9.6*	33.8**	24.8
Overall RSD ²	11.6	44.0	32.2

¹Derived from RSD of replicate measurements (Section 4.2.8.3);

²Derived from relative contributions presented in Table 5-18 using

Eq. 4-6

5.7 ML model for composition identification of SRF based on prevalent polymers

At this section the results obtained from the development of ML model for the composition identification of SRF based on seven prevalent polymers through DoE2 is presented, addressing the research objective (O4). The results are presented in a similar order to the description of DoE2 (Section 4.3).

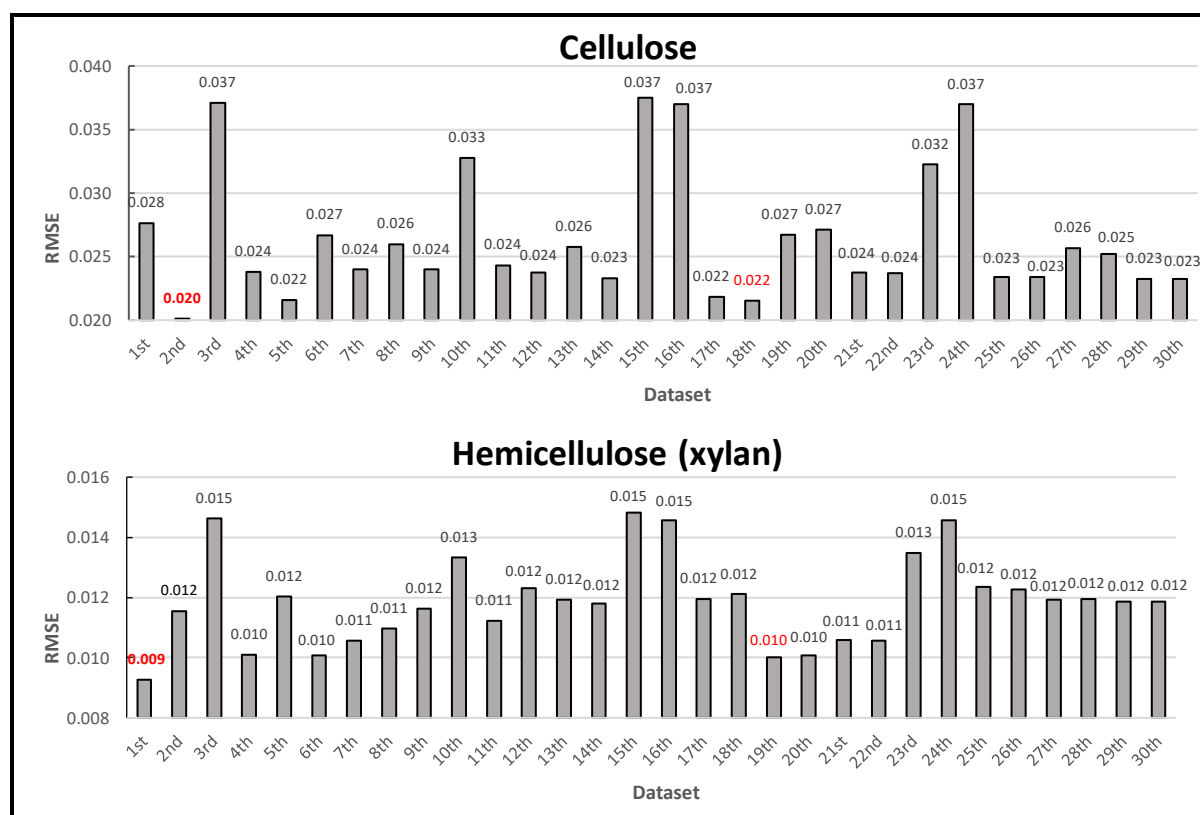
5.7.1 Model training under constant *mtry* for all dataset combinations

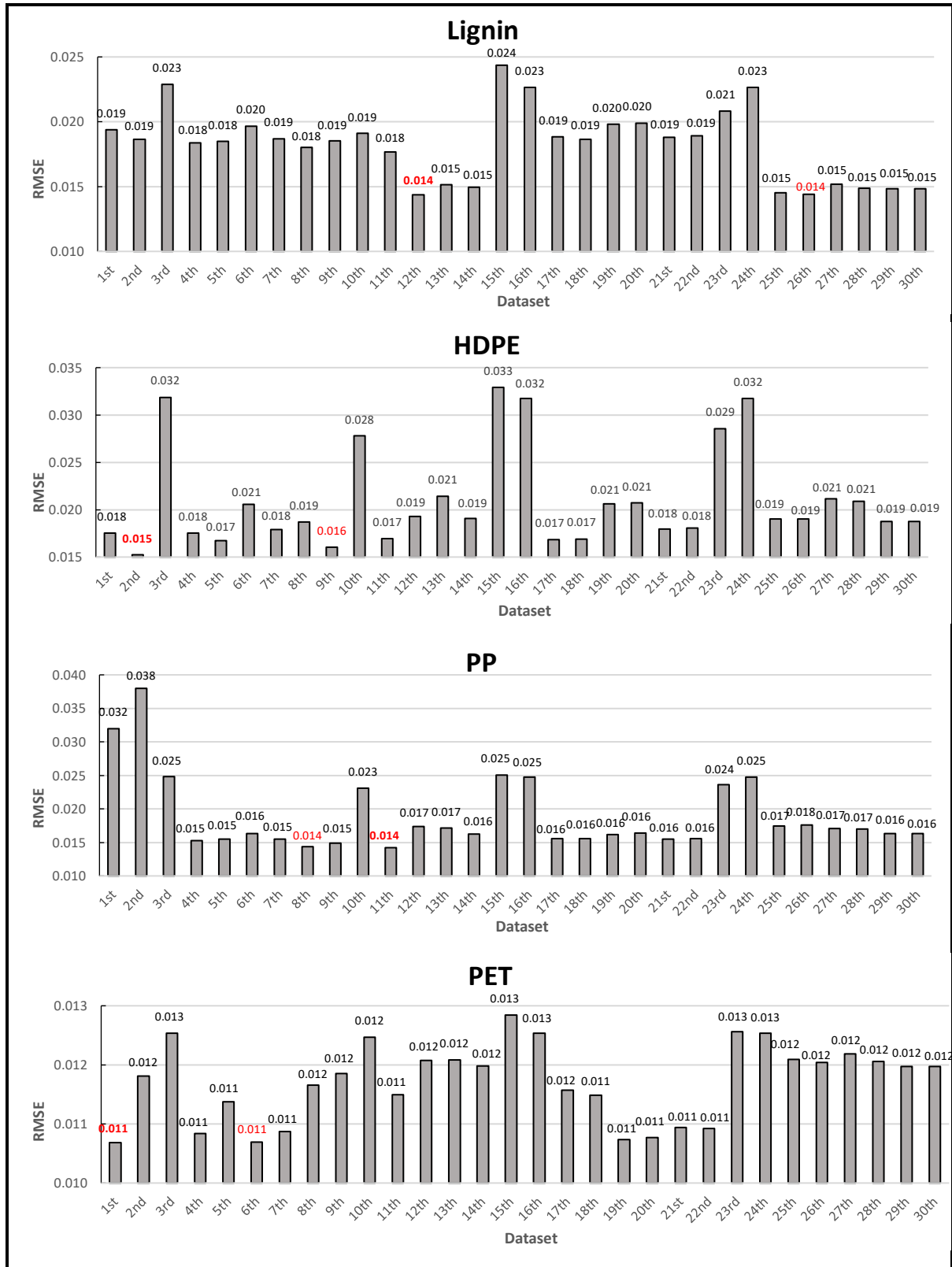
Figure 5-22 illustrates the RMSE obtained from MRF regression for all dataset combinations (**Table 4-10**) for each component following the first approach of model training – under constant tuning parameters. Related scatter plots are presented in the **Supporting Information (SI.3)**. The best dataset combination in terms of minimum RMSE is different for each component, while the weakest prediction performance is found more or less in the single FTIR datasets including raw (3rd), normalized (10th) and/or smoothed (15th, 16th, 23rd, and 24th) sets for all polymers.

The best dataset combination for cellulose identification is the 2nd (Raw TGA) followed by the 18th (TGA-FTIR_SG) dataset (**Figure 5-22**). For xylan identification (**Figure 5-22**), the best combinations

are 1st (Raw DTG) and 19th (DTG-FTIR_MA). For lignin (**Figure 5-22**), the best combinations include results from all analytical techniques – TGA, DTG, and FTIR: 12th (Normalised TG-FTIR) followed by 26th (Normalised DTG-FTIR_MA).

Quite similar to cellulose results can be found for HDPE identification (**Figure 5-22**), where single TGA datasets including the 2nd (Raw TGA) and 9th (Normalised TGA) give the lowest RMSE. In PP, the lowest RMSE is observed for the 11th (Normalised TG-DTG) and 8th (Normalised DTG) dataset indicating that normalization might give better prediction results for PP identification, likewise in case of lignin. For PET identification – a polymer at low concentrations in the plastic fraction of SRF – the best combinations were the 1st dataset (Raw DTG) and the 6th combination (Raw DTG-FTIR) which are in agreement with the results of xylan identification – a biopolymer at low concentrations in the biomass fraction of SRF. Similarly to the results of the less prevalent polymers in SRF (xylan and PET), where the lowest RMSE occurs in dataset combinations including DTG, the best datasets for PVC identification are the 1st (Raw DTG) and the 4th (Raw TG-DTG).





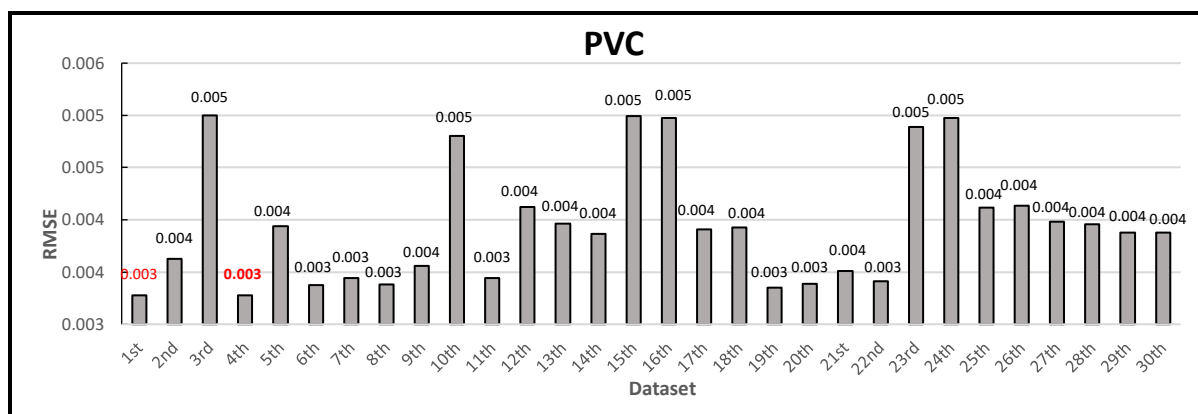


Figure 5-22. Model training with synthetic mixtures: RMSE of each prevalent SRF polymer versus all possible dataset combinations (30 in total) obtained from MRF regression analysis under constant tuning parameters (*mtry*: 10; *Ntree*: 500; *Min_Leaf*: 3) to identify the input training matrix with the minimum RMSE and therefore the best dataset for the identification of each component aiming to develop a ML model for composition identification of SRF based on prevalent polymers. Note: the red values indicate the dataset with the lowest RMSE and therefore the best dataset combination for identification of the respective component.

Figure 5-23 can be used for comparing the model performance between polymers. **Figure 5-23** presents SMAPE and RRSE from MRF regression for each raw dataset combination (from 1st to 7th) considering all prevalent polymers simultaneously following the first approach of model training.

Figure 5-23 shows that the use of FTIR results (3rd dataset) as training set gives the worst model performance, which was also confirmed by **Figure 5-22**. The 5th dataset (TG-FTIR) comes next, since errors are higher for the polymers with weaker prediction (xylan and PVC) compared to other datasets. The 1st (DTG) and the 2nd (TGA) could be a choice of input training set, but the prediction error for PP is considerably higher than raw datasets. For the other three datasets left (4th, 6th, 5th and 7th), the results are quite similar but the 4th dataset is slightly better since RRSE is lower for cellulose, lignin, HDPE, and PVC.

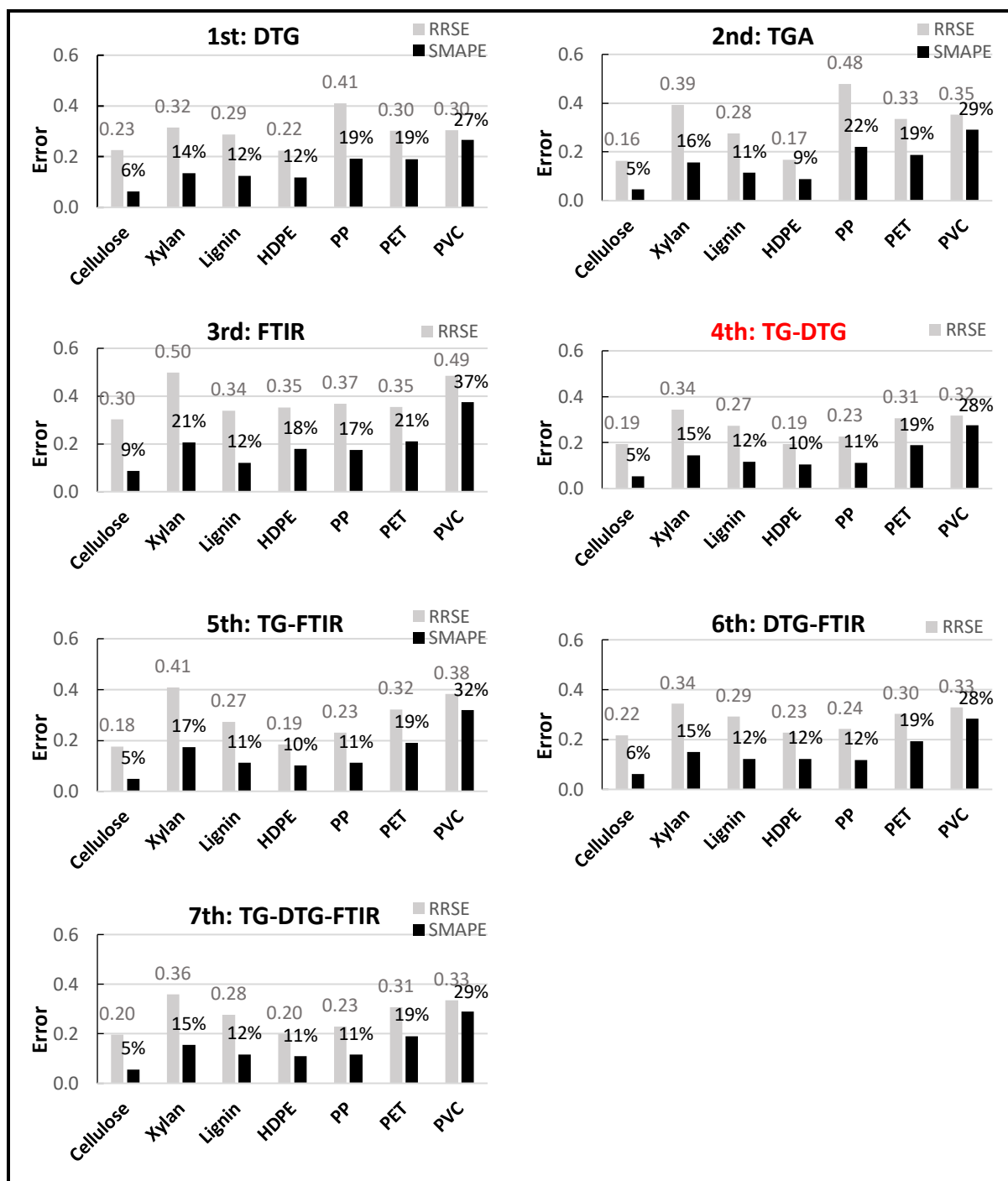


Figure 5-23. Model training with synthetic mixtures: SMAPE and RRSE for each raw dataset combination (from 1st to 7th dataset) including all prevalent polymers obtained from MRF regression analysis under constant tuning parameters (*mtry*: 10; *Ntree*: 500; *Min_Leaf*: 3) to identify the raw dataset with the minimum error respecting all prevalent polymers. Note: the red title indicates the raw dataset with the minimum combination of errors for all prevalent polymers and therefore the best raw dataset for multivariate identification of prevalent polymers in SRF.

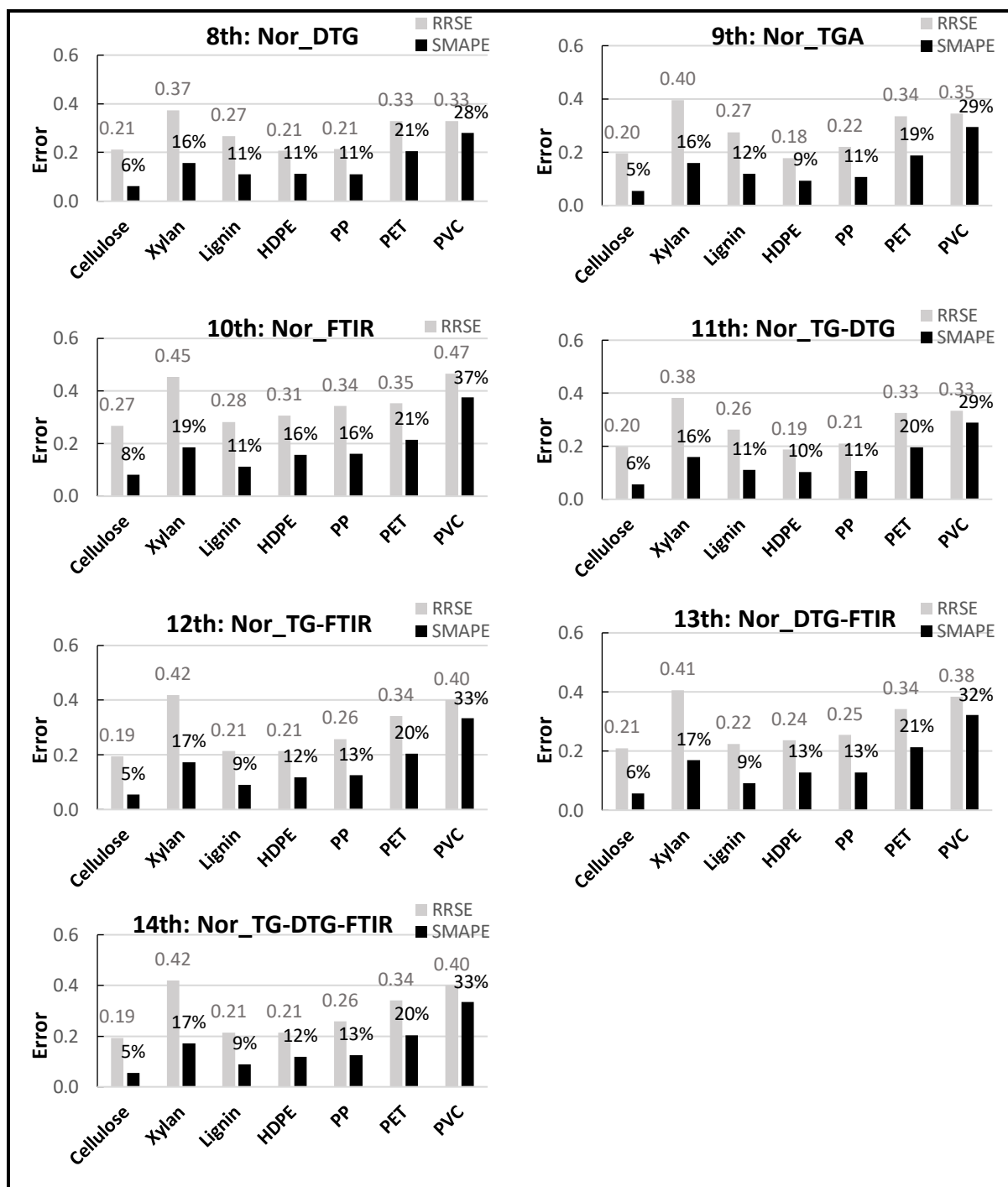


Figure 5-24. Model training with synthetic mixtures: SMAPE and RRSE for each normalised dataset combination (from 8th to 14th dataset) including all prevalent polymers obtained from MRF regression analysis under constant tuning parameters (*mtry*: 10; *Ntree*: 500; *Min_Leaf*: 3) to identify the raw dataset with the minimum error respecting all prevalent polymers.

Similarly, **Figure 5-24** presents the RRSE and SMAPE for each normalised dataset combination (from 8th to 14th) considering all prevalent polymers simultaneously. Normalised dataset have poorer performance than raw datasets (**Figure 5-23**) regarding the identification of polymers with low

proportions including xylan, PET, and PVC. For the most prevalent polymers, HDPE and cellulose, the prediction error between normalized and raw datasets is quite similar. Normalised datasets provide better model performance for lignin identification since SMAPE has a range of 9-11% and RRSE 0.21-0.28, while in raw datasets for lignin (**Figure 5-23**) SMAPE and RRSE have a range of 11-15% and 0.27-0.34, respectively. In case of PP, errors fluctuate at lower levels for normalized (**Figure 5-24**) than raw datasets (**Figure 5-23**).

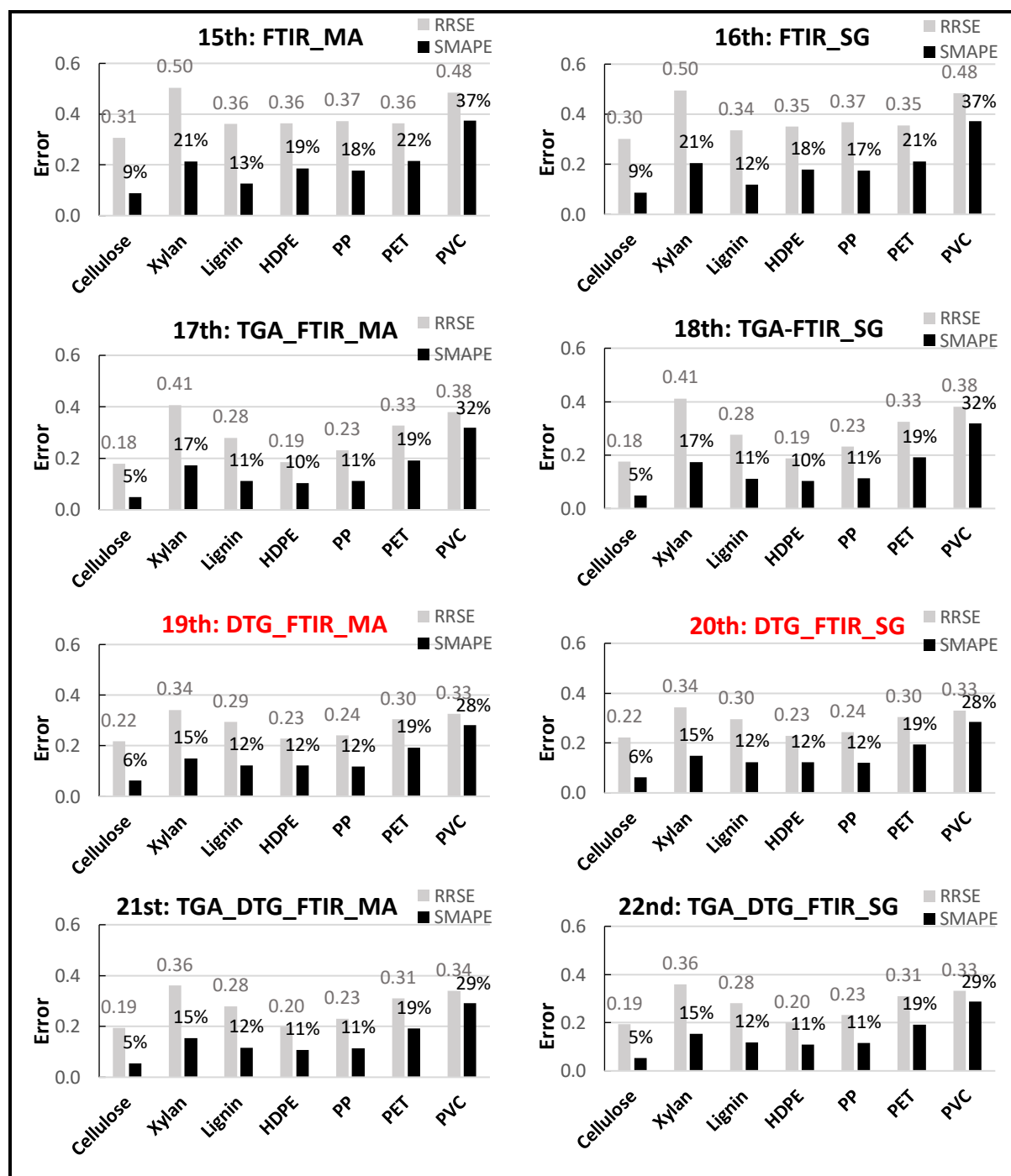
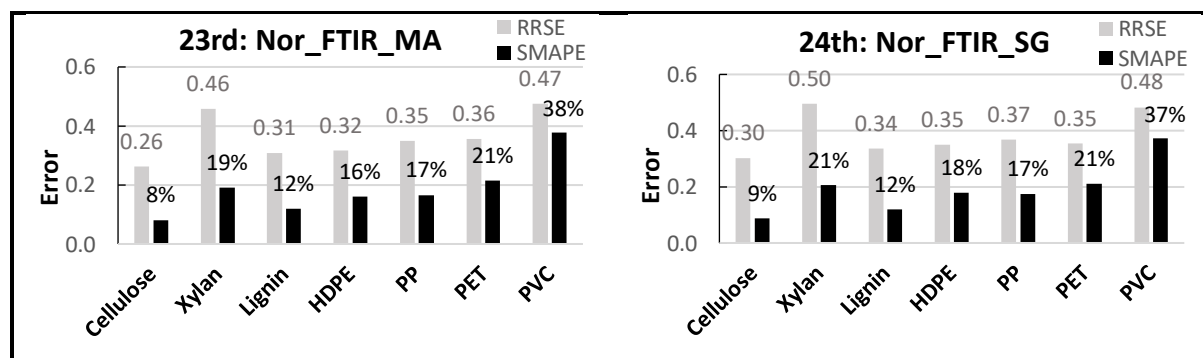


Figure 5-25. Model training with synthetic mixtures: SMAPE and RRSE for each smoothed dataset combination (from 15th to 22nd dataset) including all prevalent polymers obtained from MRF regression analysis under constant tuning parameters (*mtry*: 10; *Ntree*: 500; *Min_Leaf*: 3) to identify the raw dataset with the minimum error respecting all prevalent polymers. Note: the red title indicates the smoothed dataset with the minimum combination of errors for all prevalent polymers and therefore the best smoothed dataset for multivariate identification of prevalent polymers in SRF.

In addition, **Figure 5-25** presents the RRSE and SMAPE for each smoothed dataset combination (from 15th to 22nd) considering all prevalent polymers simultaneously. By comparing the single raw FTIR dataset (3rd) from **Figure 5-23** with the single smoothed FTIR datasets (15th and 16th) from **Figure 5-25**, it is revealed that smoothing techniques induce a slight drop of RRSE for the prediction of PVC (from 0.49 to 0.48). However, Moving-average (15th) induced a slight increase of RRSE for lignin, HDPE, PP, and PET compared to raw FTIR (3rd). No considerable difference is observed between raw and smoothed dataset combinations that contain analytical results from TGA and/or DTG. From smoothed datasets (15th-22nd), 19th and 20th dataset combination give the most improved multivariate prediction.

Following the first approach of model training, **Figure 5-26** presents the RRSE and SMAPE for each smoothed normalised dataset combination (from 15th to 22nd). By comparing the single normalised FTIR dataset (8th) from **Figure 5-24** with the single smoothed normalised FTIR datasets (23rd and 24th) from **Figure 5-26**, it is revealed that smoothing techniques do not improve the model prediction. Normalised dataset combinations (15th-22nd and 23rd-30th) give poorer performance than the respective non-normalised datasets (1-7th and 8th-14th) and therefore they are not selected for model training.



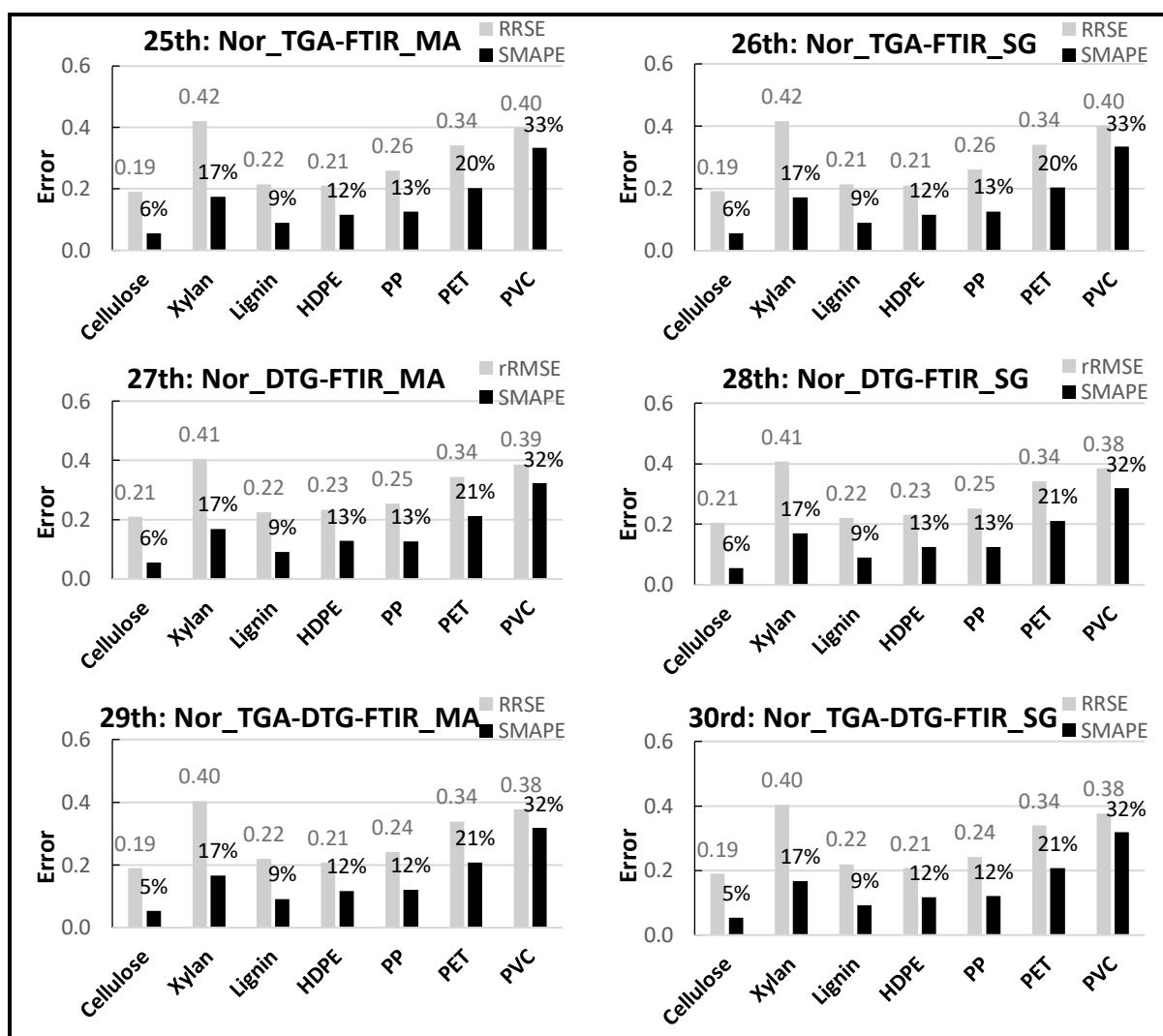
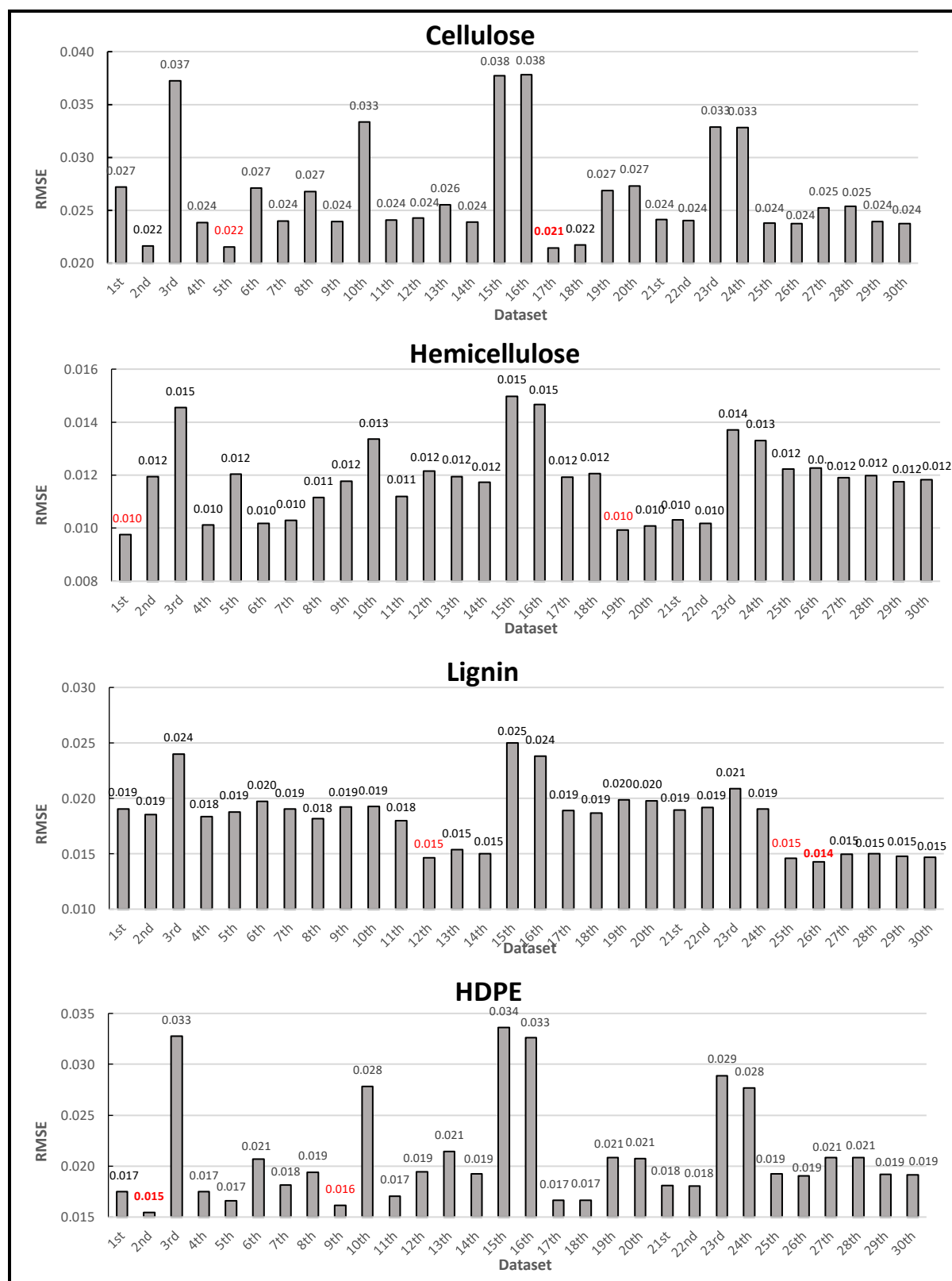


Figure 5-26. Model training with synthetic mixtures: SMAPE and RRSE for each smoothed normalized dataset combination (from 23rd to 30th dataset) including all prevalent polymers obtained from MRF regression analysis under constant tuning parameters (*mtry*: 10; *Ntree*: 500; *Min_Leaf*: 3) to identify the raw dataset with the minimum error respecting all prevalent polymers.

5.7.2 Model training under variable *mtry* depending on number of predictors

Figure 5-27 illustrates the RMSE obtained from MRF regression for all dataset combinations (**Table 4-10**) for each component following the second approach of model training – under variable *mtry* depending on the number of predictors which is variable for different dataset combinations. Related scatter plots are presented in the **Supporting Information (SI.3)**. The results of the second approach (**Figure 5-27**) are similar to the results of first approach (**Figure 5-23**), but some realignments are observed for two polymers including cellulose and PET indicating the superiority of combination of two datasets compared to single datasets. For example, for cellulose the best dataset includes the combination of TGA and FTIR results (17th and 5th) instead of single TGA (2nd) found in the first

approach. Similarly, for PET identification, a combination of DTG and FTIR (6th and 20th) give a better model performance than single DTG (1st) obtained by the first approach.



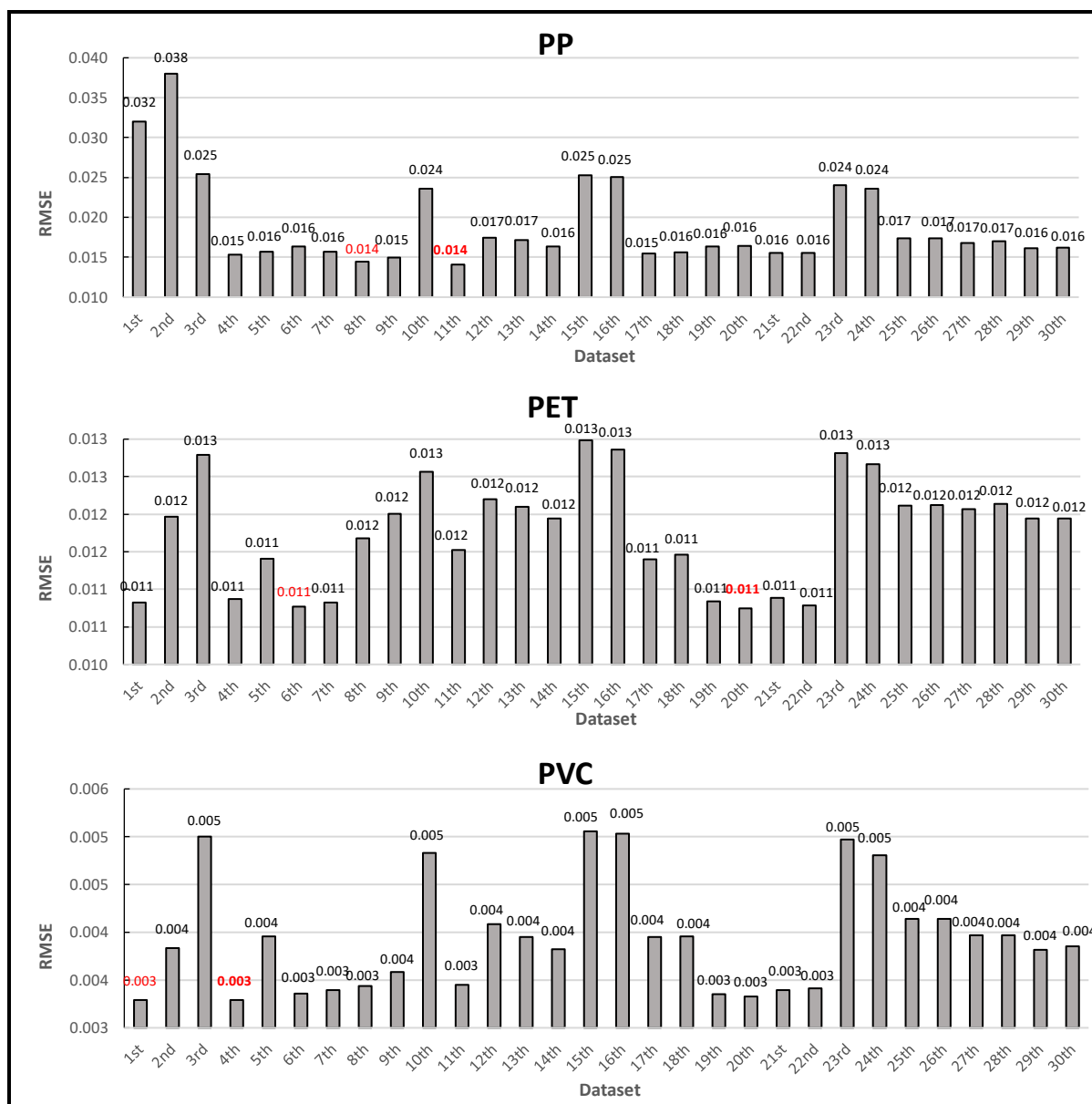
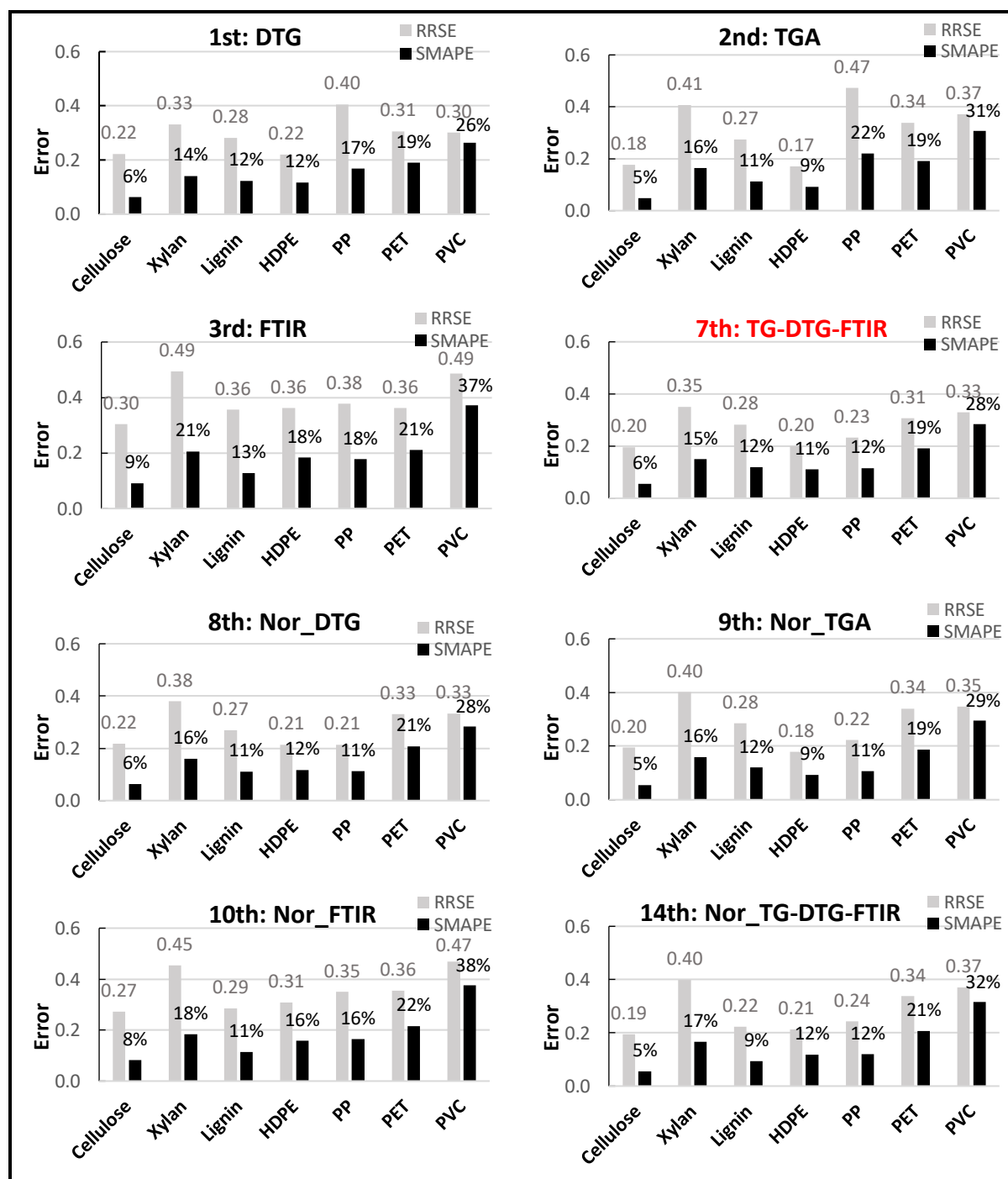


Figure 5-27. Model training with synthetic mixtures: RMSE of each prevalent SRF polymer versus all possible dataset combinations (30 in total) obtained from MRF regression analysis under variable *mtry* depending on the number of predictors (*mtry*: 5, 10, or 15; *Ntree*: 500; *Min_Leaf*: 3) to identify the input training matrix with the minimum RMSE and therefore the best dataset for the identification of each component aiming to develop a ML model for composition identification of SRF based on prevalent polymers. Note: the red values indicate the dataset with the lowest RMSE and therefore the best dataset combination for identification of the respective component.

Figure 5-28, that shows the RRSE and SMAPE for raw dataset combinations following the second approach of model training, does not considerably differ from the corresponding results of the first approach (**Figure 5-23** – **Figure 5-26**). Datasets that include a combination of two techniques (4th, 5th, and 6th) are not presented since the results are identical with these of the first approach – *mtry* is equal to 10 for both approaches. However, in the most wide dataset combinations (7th, 14th, 21st, and 22nd)

that include analytical results from three analytical techniques (12,243 predictors), RRSE and SMAPE tends to slightly decrease compared to the first approach, while in single datasets (1st-3rd, 8th-10th, 15th, 16th, 23rd and 24th having 3,601-4,321 predictors), errors have an upward trend. Thus, 7th, 21st and 22nd datasets (**Figure 5-28**) are considered as potentially suitable input training matrices for multivariate predictions along with the 4th dataset, that still slightly outperforms all dataset combinations (**Figure 5-23**).



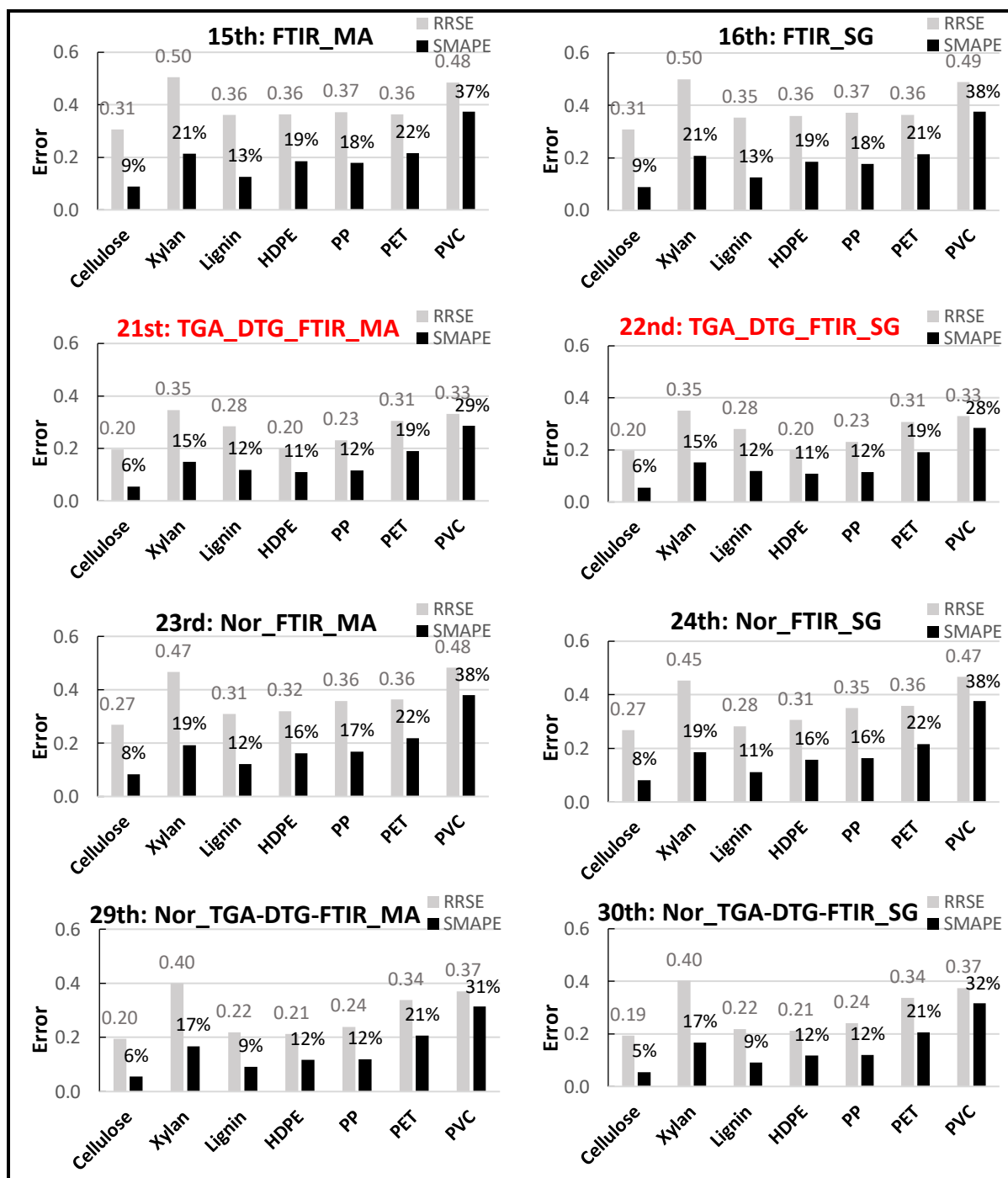


Figure 5-28. Model training with synthetic mixtures: SMAPE and RRSE for each dataset combination (from 1st to 30th dataset) including all prevalent polymers obtained from MRF regression analysis under variable *mtry* depending on the number of predictors (*mtry*: 5, 10, 15; *Ntree*: 500; *Min_Leaf*: 3) to identify the input training matrix with the minimum error respecting all prevalent polymers. Note: i) the red title indicates datasets with the minimum combination of errors for all prevalent polymers and therefore the potentially optimum raw dataset for multivariate identification of prevalent polymers in SRF; ii) graphs for datasets with a combination of two analytical techniques (4th-6th, 11th-13th, 17th-20th, 25th-28th) are omitted since they are identical with these of the first approach (*mtry* = 10).

5.7.3 Cross-validation for the three of the best dataset combinations

Table 5-20 summarises the results obtained from model training using MRF regression algorithm following the two different approaches (constant and variable *mtry*). **Table 5-20** shows that all analytical techniques (TGA, DTG, and FTIR) play a considerable role in composition identification considering only one polymer each time. Specifically, a combination of TGA with FTIR is better for cellulose and lignin, DTG with FTIR for xylan and PET, TG-DTG for PVC, and TGA for HDPE.

Simultaneously considering all polymers for each dataset, 4th, 7th, and 19th-22nd datasets provided a lower combination of prediction errors for all components (SMAPE and RRSE) than other datasets and therefore they constitute the candidates for the input training matrix of the model. The 4th dataset can be considered slightly better than others with respect to the minimum combination of errors for identification of all polymers compared to 7th and 19th-22nd. However, it is not selected for the next step of model training for two reasons: i) it is the best dataset only for PVC identification due to its considerably different TG-DTG thermogram compared to other fossil-based plastics (Heikkinen et al., 2004), while TGA-FTIR and DTG-FTIR are the best for the identification of two polymers each; and ii) FTIR is necessary to be included in the training set since it is the only technique that provides evidence on the presence of Cl in the mixtures.

Datasets 19th and 20th include actually the same analytical results (DTG and FTIR) that have been pre-processed with two different smoothing FTIR techniques having almost identical levels of prediction error. Similarly, 7th, 21st and 22nd datasets include the combination of TGA, DTG, and FTIR techniques either raw or smoothed. For both types of datasets (DTG-FTIR and TG-DTG-FTIR), only the smoothed datasets with Savitzky-Golay technique are selected for cross-validation as single FTIR datasets revealed that Savitzky-Golay technique slightly improves the model prediction.

Therefore, the 22nd (TG-DTG-FTIR_SG) dataset and 20th (DTG-FTIR_SG) are kept for model training. In addition to them, I picked a TGA-FTIR combination (18th dataset) due to its better performance compared to 20th and 22nd for the identification of cellulose, lignin, HDPE, and PP, although its performance on xylan and PVC identification was poor compared to 20th and 22nd dataset.

Normalised datasets were excluded due their poor performance for identification of polymers at low proportions (xylan and PVC).

Table 5-20. Summary of ML model training following two different approaches that shows the best dataset combinations for both identification of each prevalent polymer in SRF and for multivariate prediction including all components indicating the candidate dataset combinations for input training matrix of model construction.

Approach of model training		Cellulose	Xylan	Lignin	HDPE	PP	PET	PVC
1) Under constant <i>mtry</i>	Best dataset combination for each polymer ¹	2 nd & 18 th	1 st & 19 th	12 th & 26 th	2 nd & 9 th	8 th & 11 th	1 st & 6 th	1 st & 4 th
	Single analytical datasets included ²	TGA & FTIR	DTG & FTIR	TGA & FTIR	TGA	TGA & DTG	DTG & FTIR	TGA & DTG
	Candidate dataset combinations for multivariate prediction ³	4 th (Raw TG-DTG), 19 th (DTG-FTIR_MA) & 20 th (DTG-FTIR_SG)						
2) Under variable <i>mtry</i>	Best dataset combination for each polymer ⁴	17 nd & 5 th	1 st & 19 th	26 th & 12 th	2 nd & 9 th	11 th & 8 th	20 th & 6 th	4 th & 1 st
	Single analytical datasets included ³	TGA & FTIR	DTG & FTIR	TGA & FTIR	TGA	TGA & DTG	DTG & FTIR	TGA & DTG
	Candidate dataset combinations for multivariate prediction ⁵	4 th (Raw TG-DTG), 7 th (Raw TG-DTG-FTIR) 21 st (TG-DTG-FTIR_MA) & 22 nd (TG-DTG-FTIR_SG)						

¹In terms of RMSE (see **Figure 5-22**); ²See **Table 4-10** for description of dataset combinations; ³In terms of SMAPE and RRSE (see **Figure 5-23** to **Figure 5-26**); ⁴In terms of RMSE (see **Figure 5-27**); ⁵In terms of SMAPE and RRSE (see **Figure 5-28**)

Figure 5-29 illustrates the RMSE and MAE after 10-fold cross-validation for the selected dataset combinations. **Figure 5-29** indicates that the 22nd dataset is the best option for identification of cellulose, PP, and PET, while 20th dataset is better for xylan and PVC – the two polymers in which the ML model yields to poorer prediction compared to other polymers. The 18th dataset was better for lignin and HDPE identification but eventually not for cellulose and PP as obtained from the first step of model training. The lower difference between MAE and RMSE is found for the 22nd dataset for most response variables (polymers), while the higher difference is observed in the 18th datasets for cellulose (0.003), xylan (0.001), and lignin (0.001) compared to other two datasets.

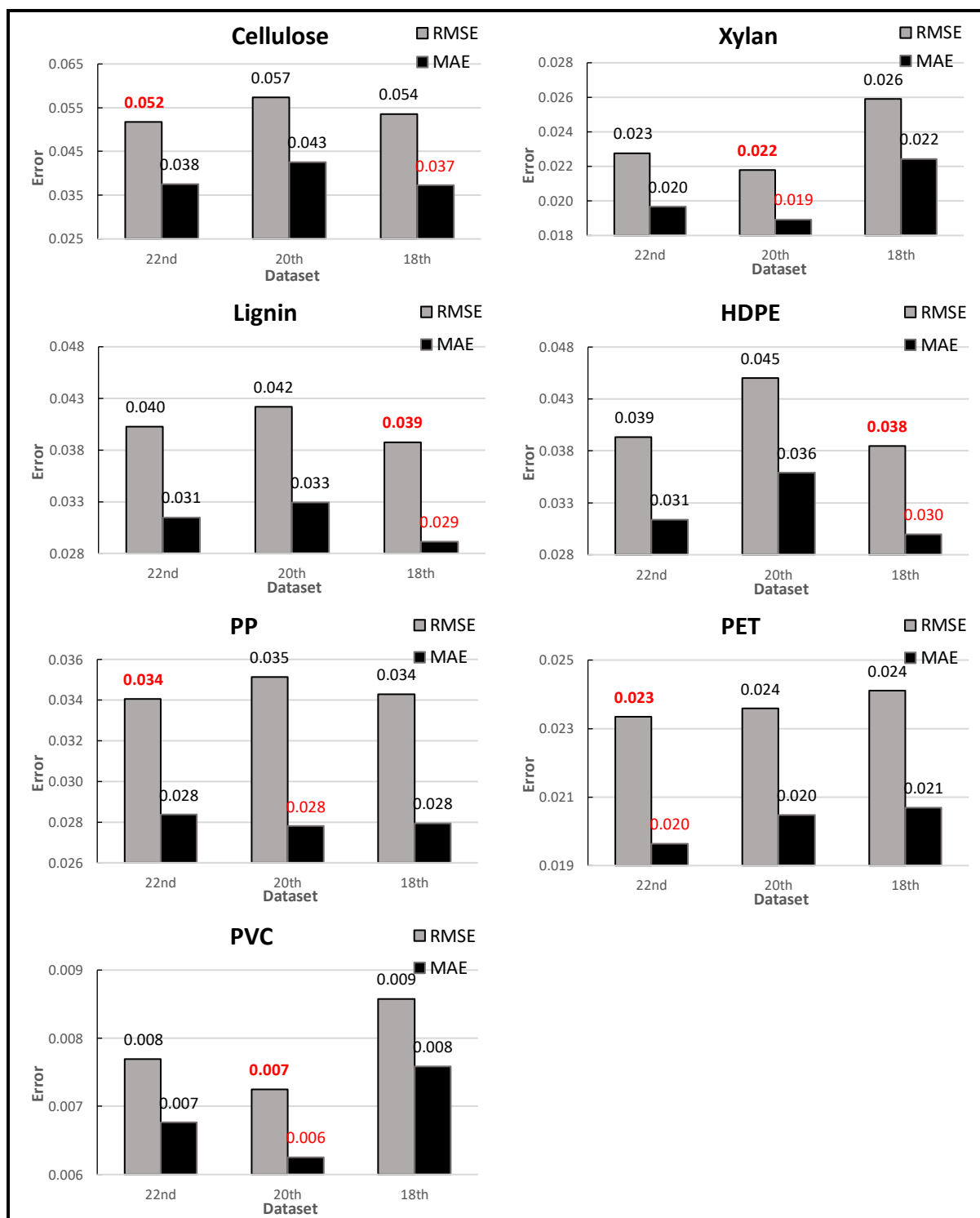


Figure 5-29. Cross-validation with synthetic mixtures: SMAPE and RRSE of each polymer obtained from 10-fold cross-validation using three selected dataset combinations (22nd, 20th, and 18th) as input training matrix in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Note: the red values indicate the dataset with the lowest errors for each component.

Figure 5-30, that shows the SMAPE and RRSE of each component for the three selected dataset combinations, provides an overview of the multivariate model prediction considering all response

variables simultaneously. In **Figure 5-30**, the poor performance of 18th dataset is clearly shown for xylan, PET and PVC (higher errors) compared to 20th and 22nd dataset and therefore it is rejected from the candidate list of the datasets for model training. Despite the better performance of the 22nd dataset from multivariate perspective, the superiority of the 20th dataset in the identification of PVC and xylan makes difficult to decide the best dataset. A compromise between the reduction of errors for responses in which model yields to poorer predictions (xylan and PVC) and the slight increase of errors in responses with relatively low errors might be preferable. In other words, it might be better to select the 20th dataset which yields to better predictions than 22nd dataset for xylan and PVC, in which model performance is poor, but the error for cellulose, lignin, PP and PET is higher. In order to select the optimum dataset for model training, hyperparameter tuning for both datasets needs to be conducted.

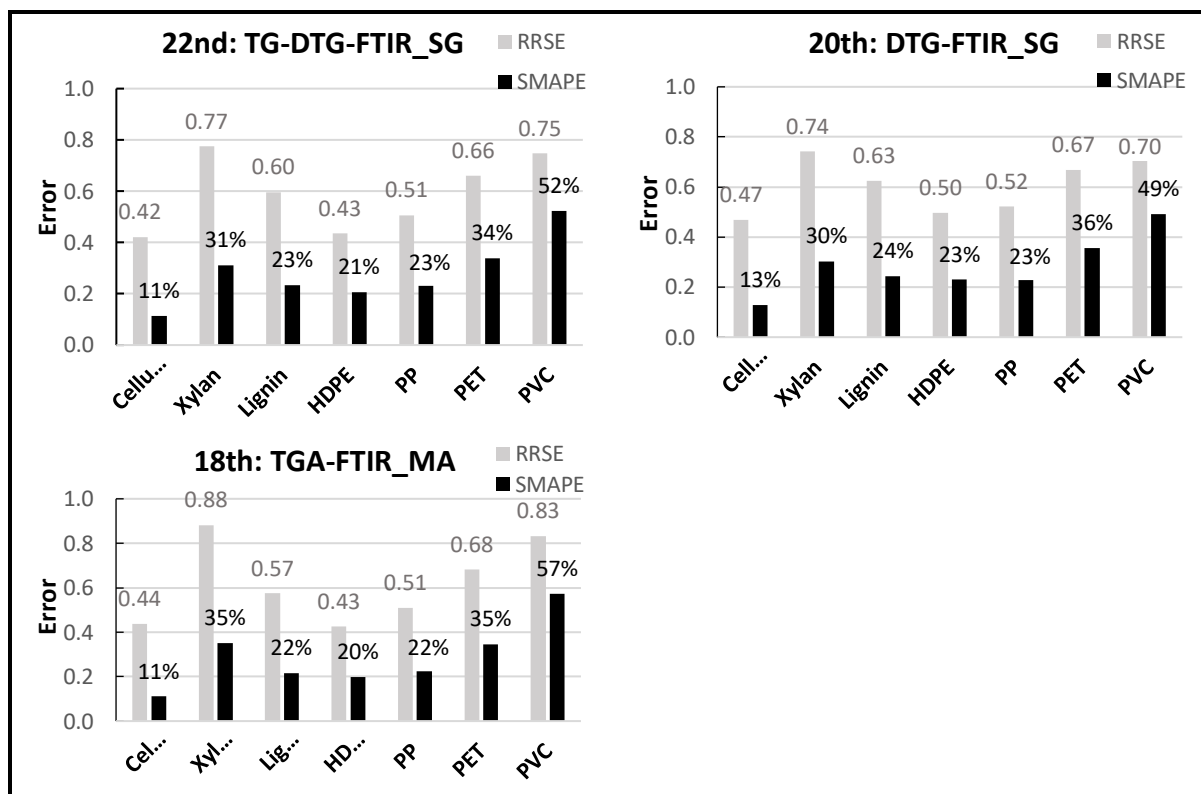


Figure 5-30. Cross-validation with synthetic mixtures: RRSE and SMAPE versus each polymer obtained from 10-fold cross-validation for the three selected dataset combinations (22nd, 20th, and 18th) as input training matrix in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers indicating the best dataset from multivariate perspective.

5.7.4 Hyperparameter tuning for two of the best dataset combinations

22nd: TG-DTG-FTIR_SG

Figure 5-31 presents the relationship of RMSE with *Ntree* for the 22nd dataset obtained from 10-fold cross-validation. Despite some fluctuations, an increase higher than 600 trees does not considerably improve the model performance. However, there is a perceptible level off for lignin, PP, and PET when *Ntree* is equal to 1,000. Therefore, the selected value for *Ntree* is 1,000 using the 22nd dataset as input training matrix.

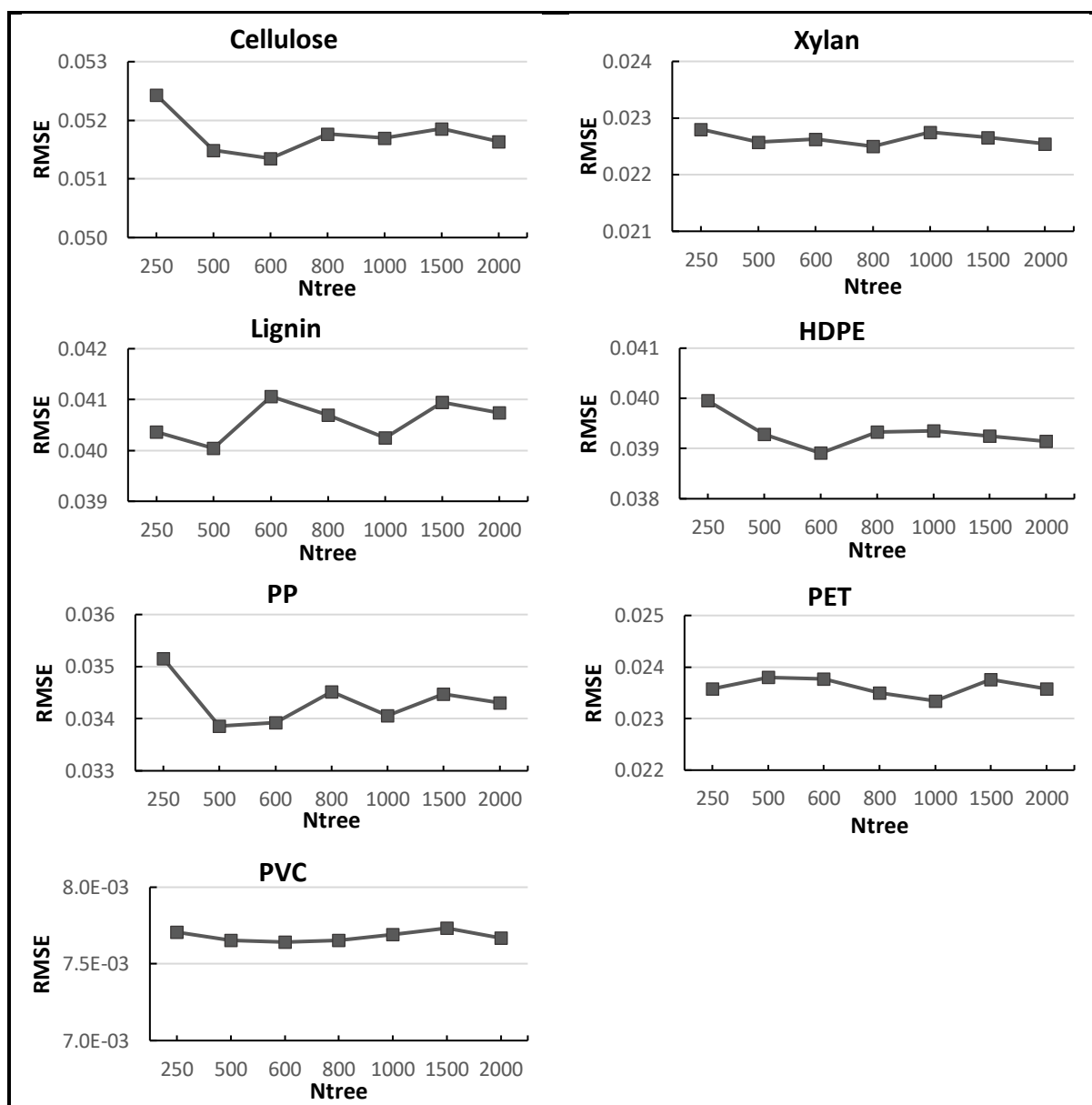


Figure 5-31. Hyperparameter tuning with 10-fold cross-validation: RMSE of each polymer versus the number of trees (*Ntree*) using the 22nd dataset (TG-DTG-FTIR_SG) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Note: *mtry* was set at 10 and *Min_Leaf* at 3. The selected value of *Ntree* was at 1,000.

Figure 5-32 presents the relationship of RMSE with *mtry* for the 22nd dataset obtained from 10-fold cross-validation. Herein, the trend of RMSE versus *mtry* is different for each component. For cellulose, HDPE, and PP the optimum *mtry* is between 10 and 15, for lignin is at the minimum value 5, for PVC is at 30, while the optimum *mtry* is significantly higher for xylan (100) and PET (50). However, the selection of high *mtry* to improve the prediction of xylan identification that is still weaker than other components would lead to considerable deterioration of model performance for the other components. By setting *mtry* at 30, the optimal compromise can be obtained (**Figure 5-32**). This low value of *mtry* compared to the number of predictors (12,243) indicates that predictors are correlated (Gareth et al., 2013).

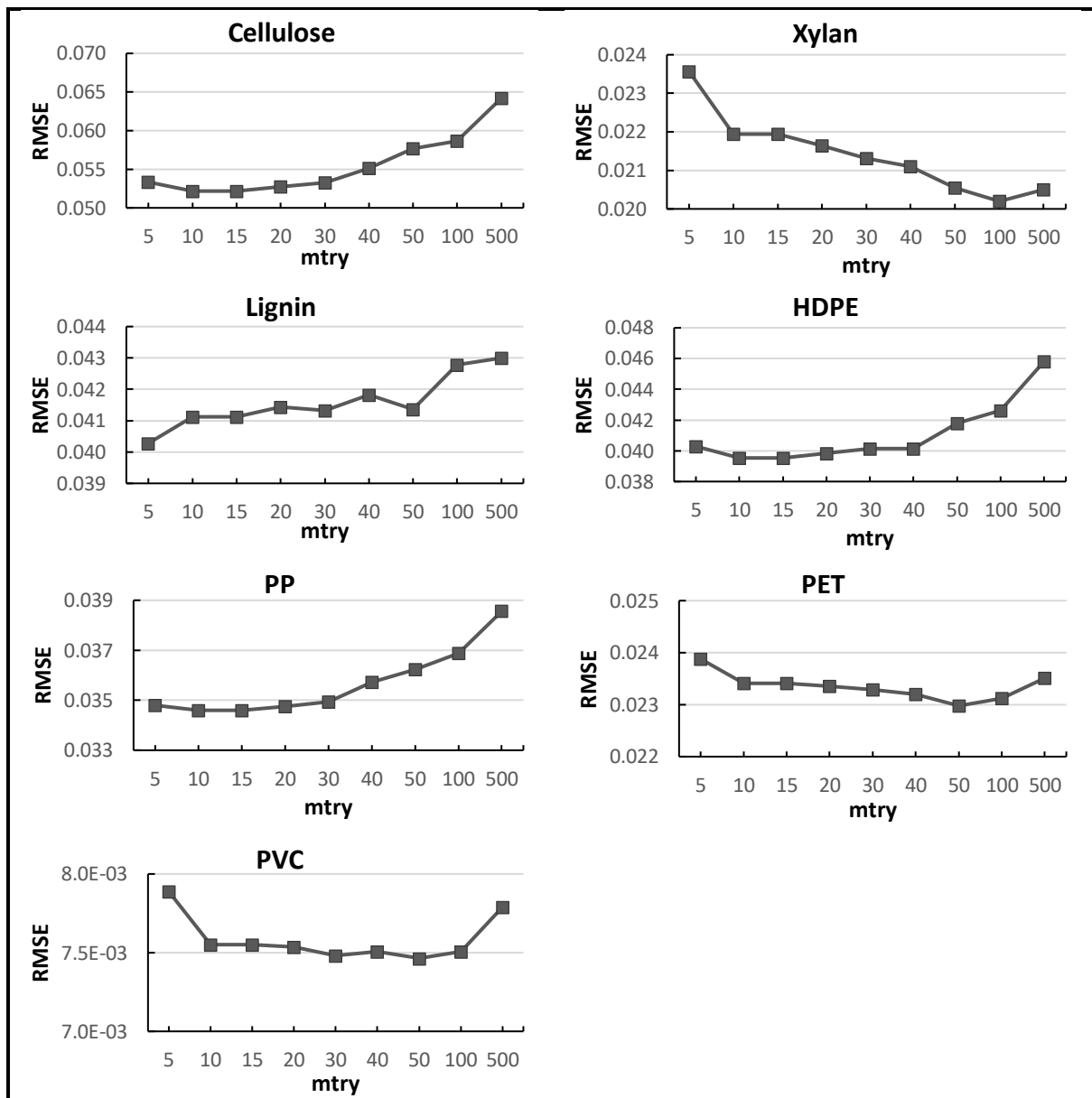


Figure 5-32. Hyperparameter tuning with 10-fold cross-validation: RMSE of each polymer versus *mtry* using the 22nd dataset (TG-DTG-FTIR_SG) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Note: *Ntree* was set at 1,000 and *Min_Leaf* at 3. The selected value of *mtry* was at 30.

Figure 5-33 presents the relationship of RMSE with *Min_Leaf* for the 22nd dataset obtained from 10-fold cross-validation. **Figure 5-33** clearly shows that the minimum value of *Min_Leaf* (= 3) is the optimal choice since RMSE is lower for all SRF polymers.

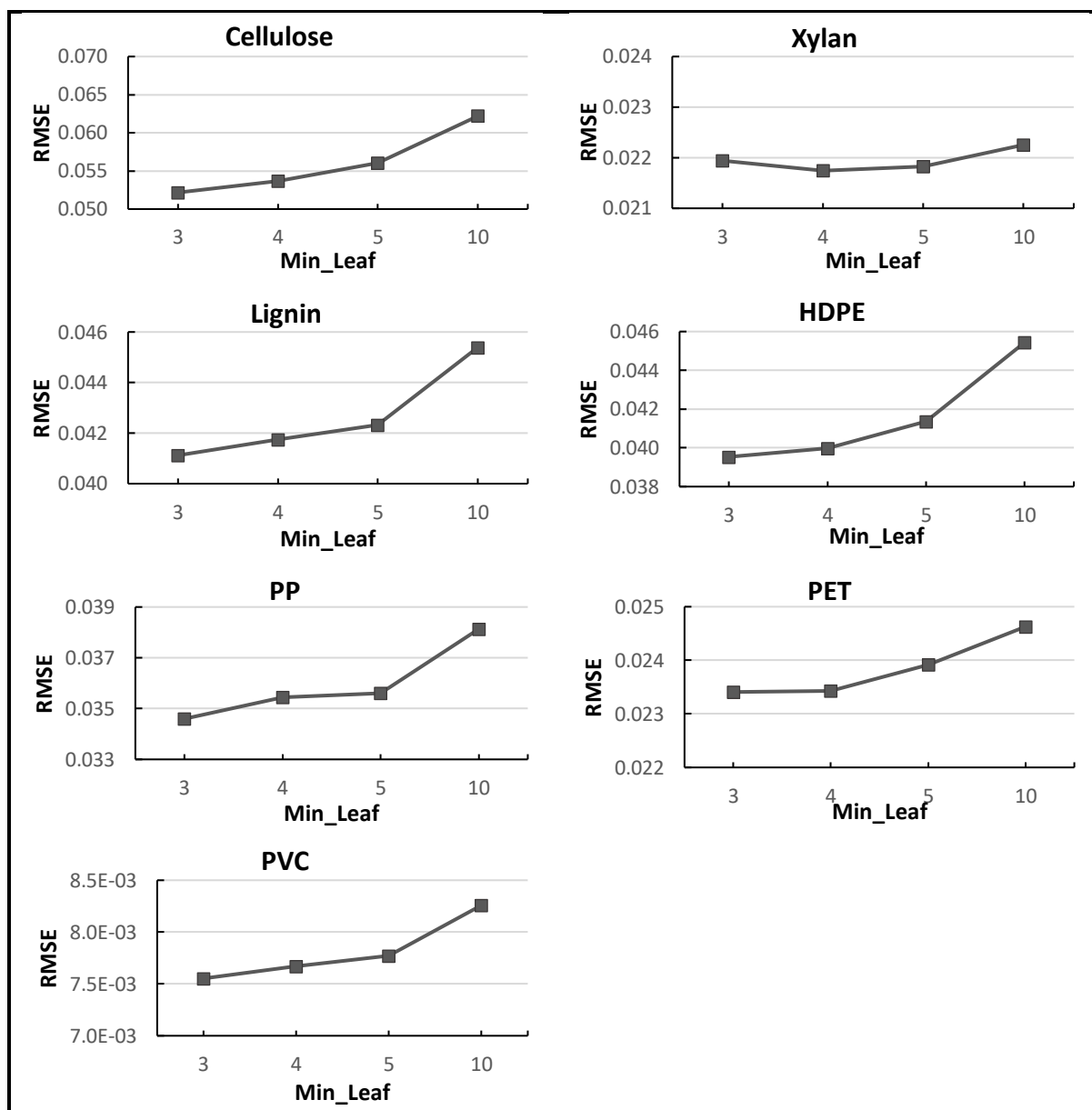


Figure 5-33. Hyperparameter tuning with 10-fold cross-validation: RMSE of each polymer versus *Min_Leaf* using the 22nd dataset (TG-DTG-FTIR_SG) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Note: *Ntree* was set at 1,000 and *mtry* at 10. The selected value of *Min_Leaf* was at 3.

20th: DTG-FTIR_SG

Figure 5-34 presents the relationship of RMSE with *Ntree* for the 20th dataset obtained from 10-fold cross-validation. Similarly to the 22nd dataset (**Figure 5-34**), setting *Ntree* higher than the default value (=500) does not considerably improves the model performance. To obtain comparative results with this of the 22nd dataset, the value of 1,000 was selected for *Ntree*.

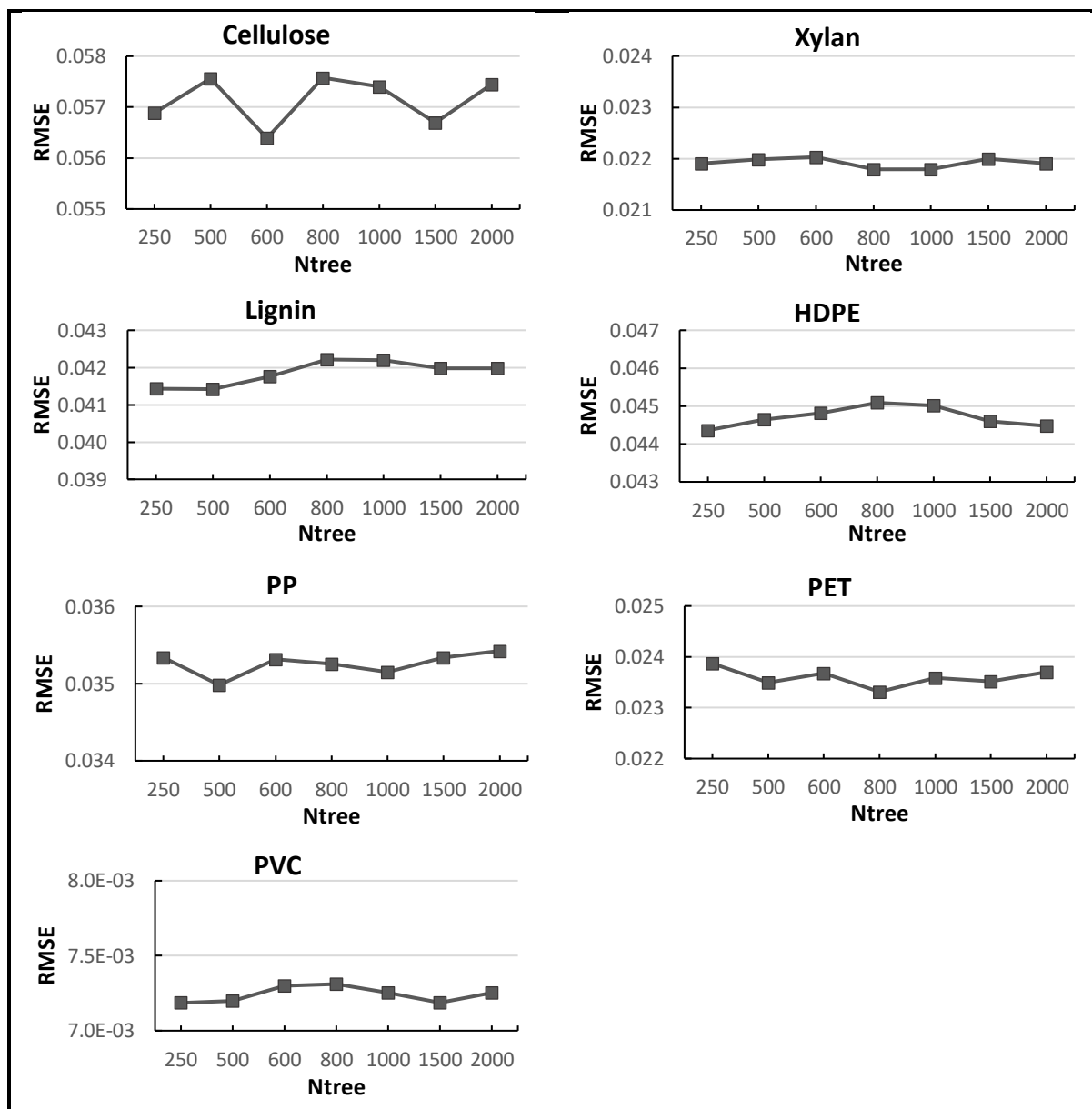


Figure 5-34. Hyperparameter tuning with 10-fold cross-validation: RMSE of each polymer versus *Ntree* using the 20th dataset (DTG-FTIR_SG) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Note: *mtry* was set at 10 and *Min_Leaf* at 3. The selected value of *Ntree* is 1,000.

Figure 5-35 presents the relationship of RMSE with *mtry* for the 20th dataset obtained from 10-fold cross-validation. Similarly to the 22nd dataset (**Figure 5-32**), the optimal *mtry* is different for each component. For cellulose, cellulose, lignin and PP the optimal *mtry* is between 5 and 10, for xylan and HDPE is 50, for PET is 100 and for PVC is 15. By setting *mtry* at 50, the optimal compromise can be obtained (**Figure 5-35**).

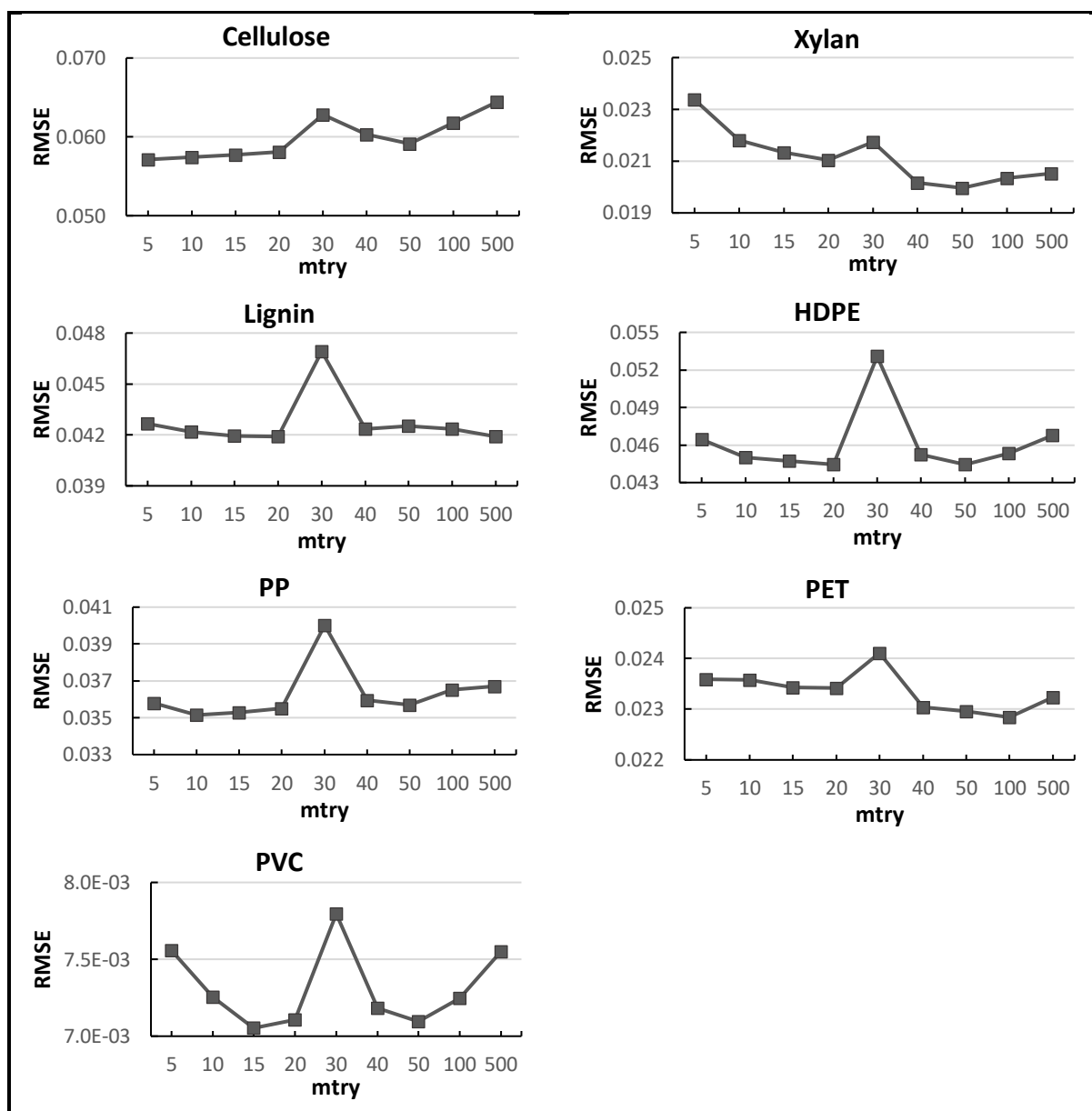


Figure 5-35. Hyperparameter tuning with 10-fold cross-validation: RMSE of each polymer versus *mtry* using the 20th dataset (DTG-FTIR_SG) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Note: *Ntree* was set at 1,000 and *Min_Leaf* at 3. The selected value of *mtry* is 50.

Figure 5-36 presents the relationship of RMSE with *Min_Leaf* for the 20th dataset obtained from 10-fold cross-validation. Contrarily to the 22nd dataset (**Figure 5-33**), **Figure 5-36** shows that the optimal *Min_Leaf* is different for each polymer. The optimal value of *Min_Leaf* is 3 for cellulose, lignin, HDPE, and PE, while for xylan, PET and PVC *Min_Leaf* is 4. The value was set at 4 since the improvement of model prediction is case of xylan and PVC is considerable, while the deterioration in case of other components is minor.

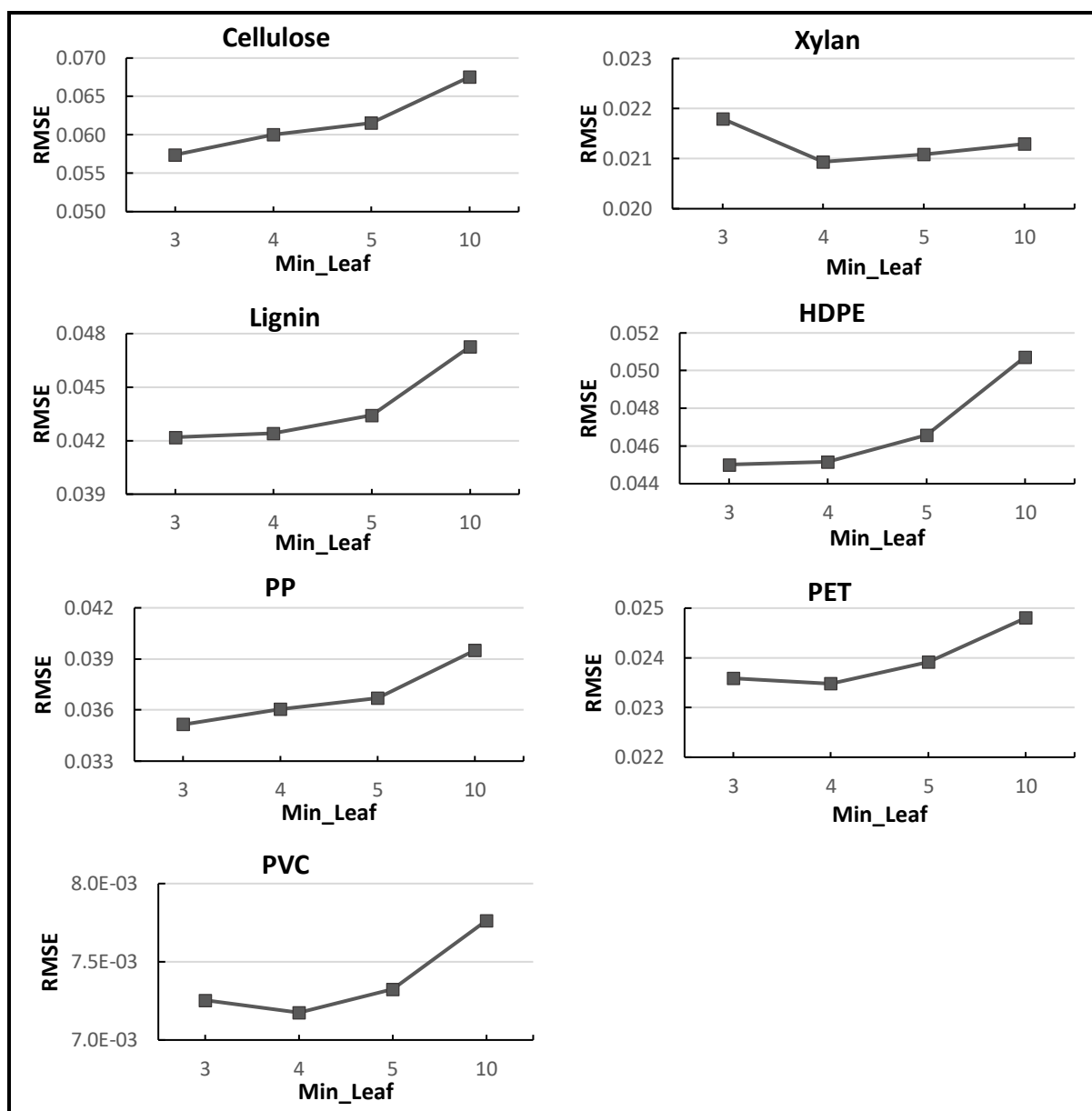


Figure 5-36. Hyperparameter tuning with 10-fold cross-validation: RMSE of each polymer versus *Min_Leaf* using the 20th dataset (DTG-FTIR_SG) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Note: *Ntree* was set at 1,000 and *mtry* at 10. The selected value of *Min_Leaf* is 4.

5.7.5 Hold-out validation with genuine SRF components for two of the best dataset combinations

Figure 5-37 illustrates the RMSE and MAE of each polymer received from the hold-out validation set using as input matrix the 22nd and 20th datasets.

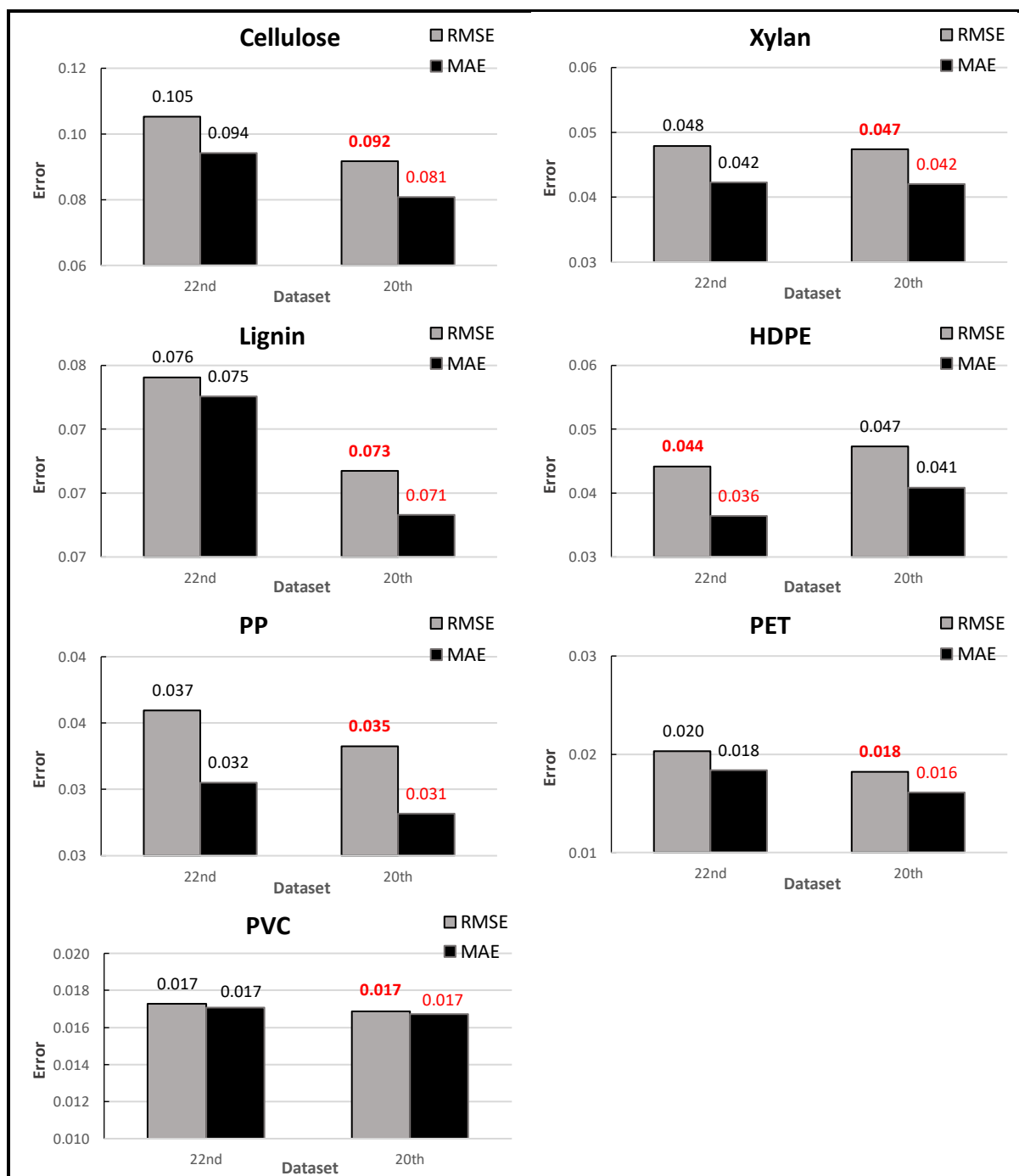


Figure 5-37. Hold-out validation with waste mixtures: RMSE and MAE of each polymer using two different datasets as input matrix (22nd and 20th) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Note: the red values indicate the dataset with the lowest errors for each component.

After detecting the optimal tuning parameters in the stage of hyperparameter tuning for both datasets – 22nd and 20th – (**Section 0**), the superiority of the 20th against the 22nd dataset is revealed (**Figure 5-37**). Excluding the identification of HDPE in which the 22nd dataset gives a better prediction (lower RMSE and MAE), the selection of 20th dataset as input validation matrix provides lower validation error for all components.

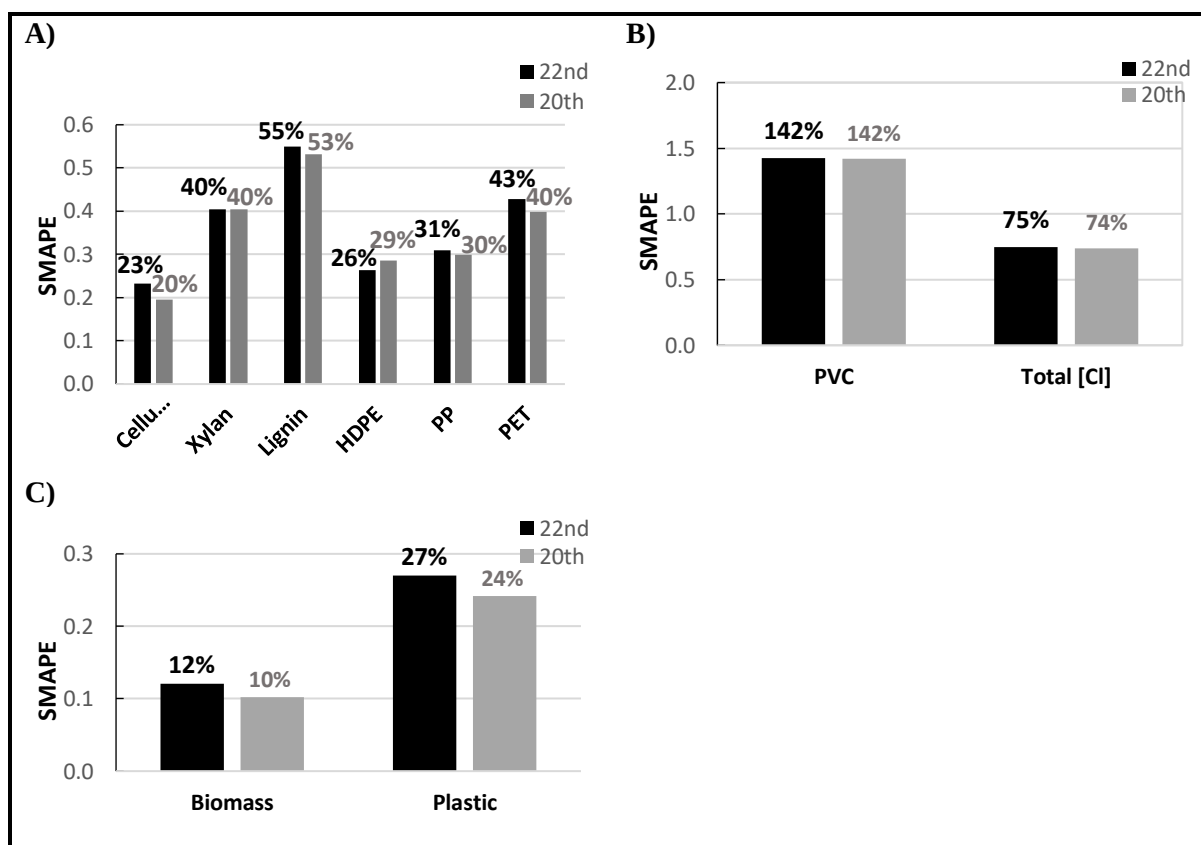


Figure 5-38. Hold-out validation with waste mixtures: SMAPE using two different datasets as input matrix (22nd and 20th) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers: A) SMAPE for identification of cellulose, xylan, lignin, HDPE, PP, and PET; B) SMAPE for identification of PVC and Total [Cl] as calculated from amounts of PVC with Total [Cl] equal to 53.7% w/w; C) SMAPE for identification of biomass and plastic fraction. Note: 20th (DTG-FTIR_SG) outperforms 22nd (TG-DTG-FTIR_SG) dataset in terms of forecast accuracy.

The better performance of the 20th dataset can also be seen by **Figure 5-38** that shows the validation error expressed as SMAPE. **Figure 5-38** offers insights into the comparison of model performance among components. In both datasets, the hold-out validation error is considerably lower for identification of cellulose (20-23%) followed by HDPE (26-29%), PP (30-31%), xylan (40%), PET (40-43%), and lignin (53-55%) (**Figure 5-38-A**). However, the forecast error exceeds an acceptable value (142%) for PVC (**Figure 5-38-B**). By matching the predicted proportions of PVC with the

corresponding Total [Cl] in the mixtures of validation set – assuming than PVC has 53.7% Total [Cl] as determined from analysis – and comparing the predicted Total [Cl] with the chemically measured Total [Cl] in the mixtures (observed values), the validation error drops to 74-75% (**Figure 5-38-B**). Beyond polymers, the validation error was calculated for the biomass (a summation of cellulose, xylan, and lignin) and plastic (a summation of HDPE, PP, PET, and PVC) fraction in hold-out validation samples (**Figure 5-38-C**). **Figure 5-38-C** shows more clearly than **Figure 5-38-A** and **Figure 5-38-B** that the 20th dataset results in better model performance than 22nd dataset.

5.7.6 Model completion

Following the steps of model training and validation, the ML model was completed using the 20th dataset as input training matrix. The code of ML algorithm build to identify the composition of SRF based on its prevalent components is provided in **Appendix F**.

Figure 5-39 summarises forecast errors expressed as SMAPE and RMSE at each stage of model development – training, cross-validation, and hold-out validation – using the 20th dataset after hyperparameter tuning. As it was expected, the minimum prediction error is observed in the stage of model training, while the highest in the stage of hold-out validation. However, errors are not substantially different between cross-validation and hold-out validation in case of biomass and plastic fraction, while RMSE are almost identical for plastic polymers and Total [Cl]. SMAPE between Total [Cl] and PVC are identical in model training and cross-validation since PVC is the exclusive source of Cl (synthetic samples). However, RMSE is different between Total [Cl] and PVC as RMSE is scale-dependent metric. For biomass fraction, SMAPE is almost equal between cross- and hold-out validation (10%), while it is higher but still comparative for plastic fraction (17% for cross-validation vs 24% for hold-out validation).

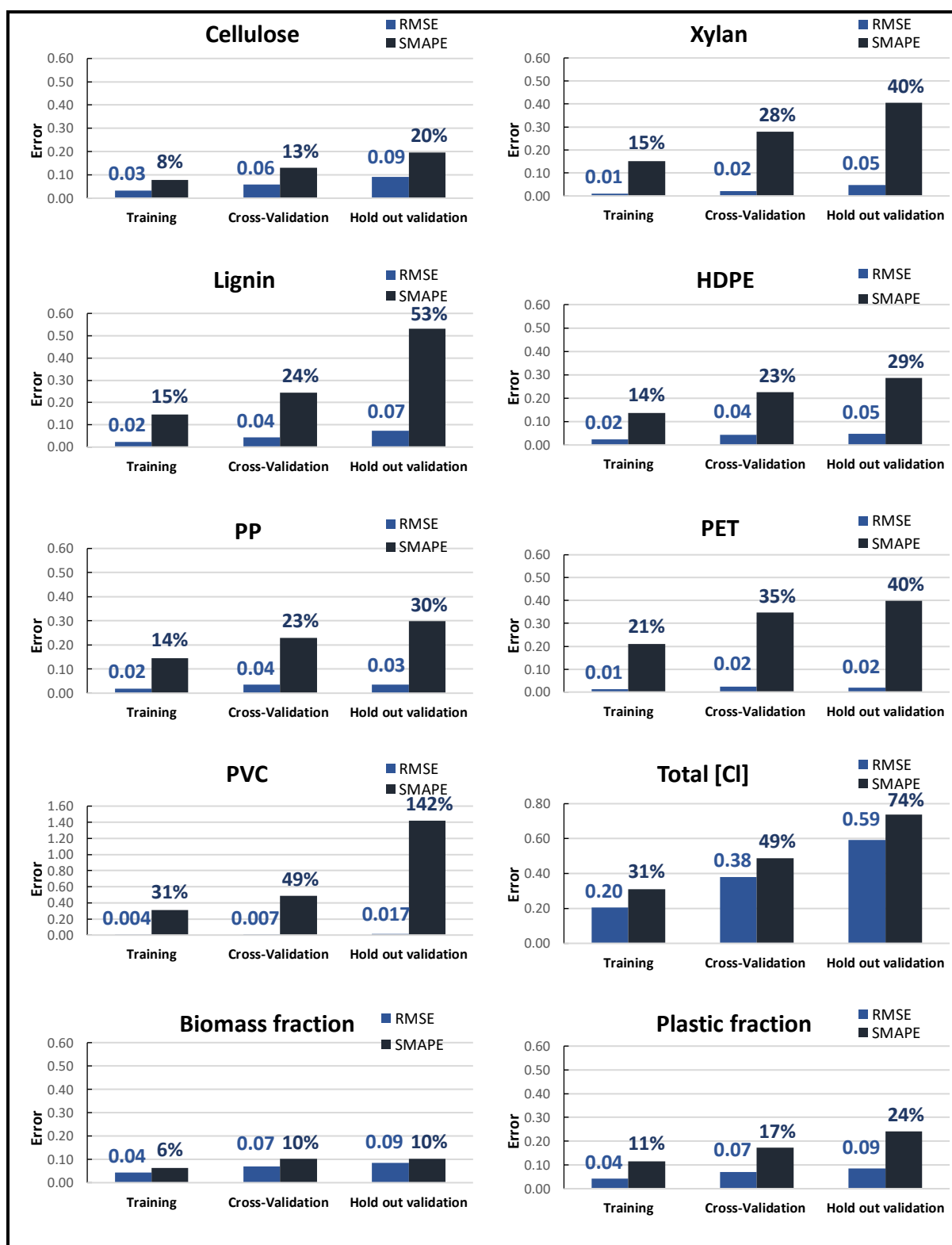
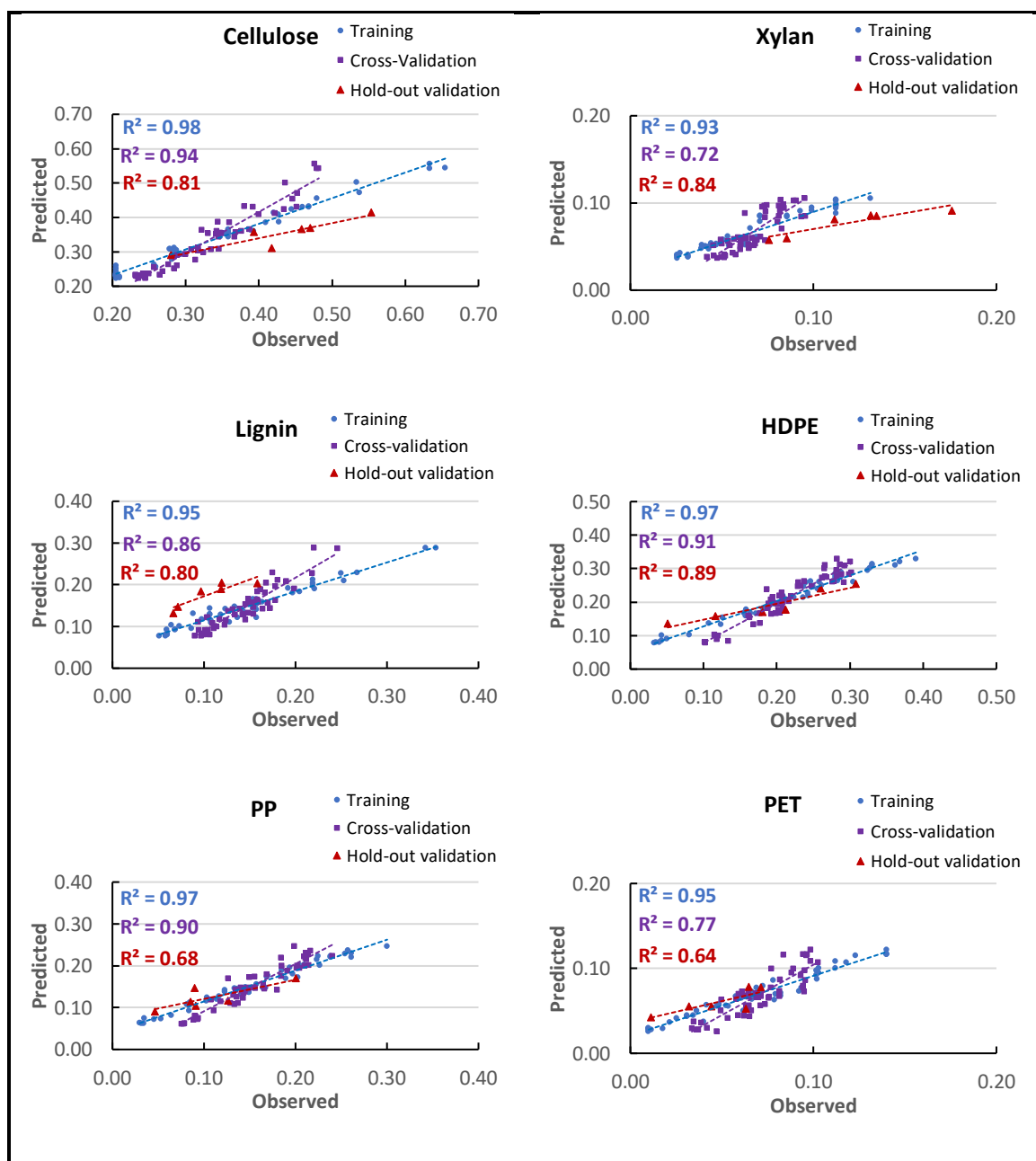


Figure 5-39. Completed model: forecast error, expressed as RMSE and SMAPE, of polymers (cellulose, xylan, lignin, HDPE, PP, PET, and PVC), Total [CI] as calculated from amounts of PVC with Total [CI] equal to 53.7% w/w, biomass and plastic fraction in the stage of training, 10-fold cross-validation and hold-out validation using the best dataset combination (20th – DTG-FTIR_SG) as input matrix and optimal tuning parameters ($N_{tree} = 1,000$, $mtry = 50$, and $Min\_Leaf = 4$) in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers.

Figure 5-40 illustrates the goodness of fit in prevalent polymers as well as Total [Cl], biomass and plastic fraction for the training, cross-validation and hold-out validation set. It is shown that data from all stages fit well in the respective trend lines apart from PVC and therefore Total [Cl] of hold-out validation. Additionally, predicted values of hold-out validation set for lignin tend to have a distance above the trend line of training.



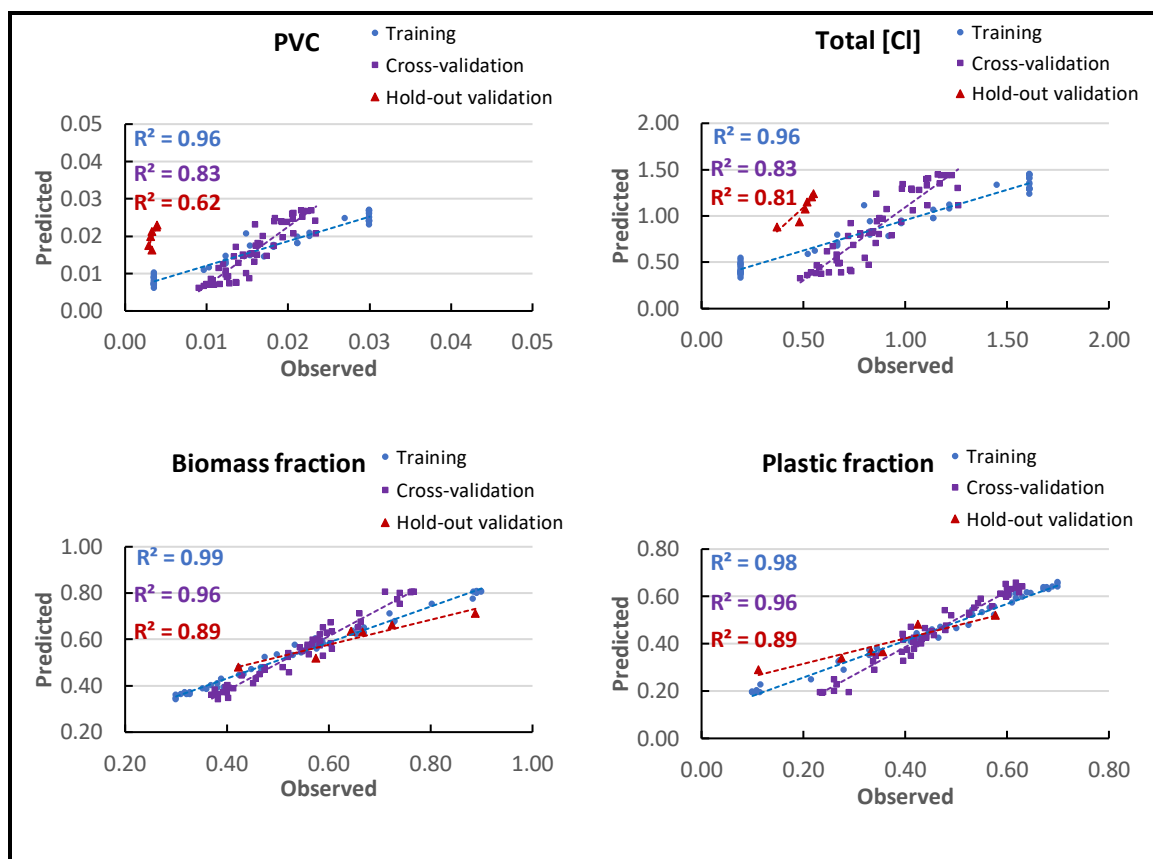


Figure 5-40. Completed model: Observed vs predicted values of prevalent polymers (cellulose, xylan, lignin, HDPE, PP, PET, and PVC), Total [Cl] as calculated from amounts of PVC with Total [Cl] equal to 53.7% w/w, biomass and plastic fraction for training, cross-validation and hold-out validation set using the best dataset combination (20th – DTG-FTIR_SG) as input matrix and optimal tuning parameters in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers.

5.7.7 Model testing with commercially produced SRF samples

Figure 5-41 presents the forecast error for identification of biomass and plastic fraction in commercially produced SRF samples obtained from model testing. RMSE is identical between biomass and plastic fraction since the samples are expressed as binary mixtures consisting of two components (biomass and plastics) which inevitably are highly correlated. SMAPE indicates that model yields to high prediction of biomass (6%) and plastic (9%) content in SRF samples, despite the presence of fines, impurities and other trace substances.

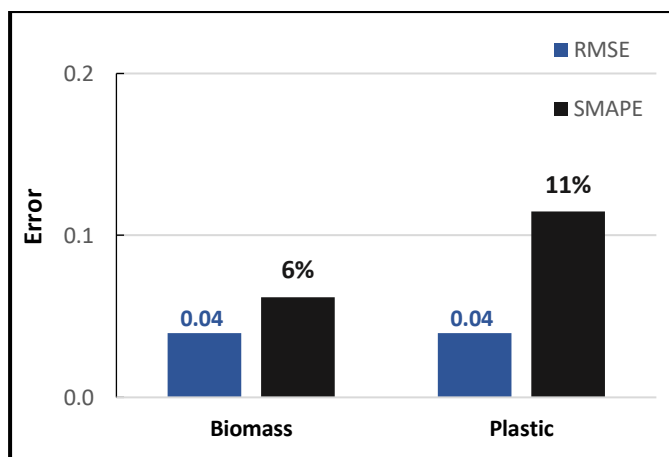


Figure 5-41. Model testing with commercially produced SRF samples: Forecast error, expressed as RMSE and SMAPE, for identification of biomass and plastic fraction using the best dataset combination (20th: DTG-FTIR_SG) as input matrix and optimal tuning parameters in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers. Biomass is considered the summation of cellulose, xylan, and lignin, while plastic is considered the summation of HDPE, PP, PET, and PVC. Note: Errors for identification of polymers were not obtained due to difficulty to accurately determine their proportions in SRF samples and therefore inability to calculate the prediction errors.

Figure 5-42 illustrates the goodness of fit in biomass and plastic fraction for the training, cross-validation and hold-out validation set. The residuals of testing set fit very well in the trend line of training.

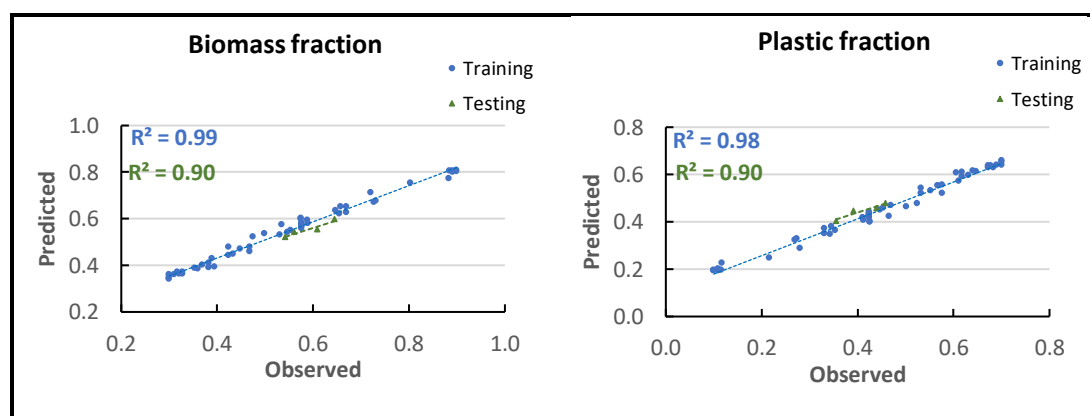


Figure 5-42. Model testing with commercially produced SRF samples: Observed vs predicted values of biomass and plastic fraction for training and testing set using the best dataset combination (20th – DTG-FTIR_SG) as input matrix and optimal tuning parameters in MRF regression analysis for the development of a ML algorithm for composition identification of SRF based on its prevalent polymers.

Following the prediction results of ML model, the composition of SRF samples based on prevalent components is shown in **Table 5-21**. In SRF1 and SRF2 collected from the same MT plant, the content of biopolymers ranges from 52.0-54.3% w/w and of fossil-based polymers 45.7-48% w/w.

Similarly, in SRF3 and SRF4 collected from the second MT plant, the content of biopolymers is slightly higher ranging from 55.3-59.7% w/w and of fossil-based fraction 40.3-44.7%. The content of PVC is slightly higher for the samples of the second plant indicating higher Total [CI], while the amount of PET is higher for the samples of the first plant.

Table 5-21. Predicted composition of commercially produced SRF samples based on prevalent polymers, accompanied by Total [CI] calculated by the predicted amount of PVC, identified by ML model.

Sample	Cellulose ¹ (% w/w)	Xylan ¹ (% w/w)	Lignin ¹ (% w/w)	HDPE ¹ (% w/w)	PP ¹ (% w/w)	PET ¹ (% w/w)	PVC ¹ (% w/w)	Total [CI] (% w/w) ^{1,2}
SRF1	32.44	6.16	15.72	22.64	13.40	7.78	1.86	1.00
SRF2	31.48	5.71	14.85	23.78	14.13	8.24	1.80	0.97
SRF3	33.51	6.60	15.19	21.91	13.95	6.94	1.90	1.02
SRF4	35.62	7.18	16.91	19.67	12.21	6.40	2.00	1.08

¹Expressed on as received basis: after pre-drying to be subjected to TG-DTG; ²Assuming that Total [CI] in PVC is equal to 53.7% w/w as obtained from measurements

5.7.8 A comparison of ML model with TGA and manual sorting for determination of biomass and plastic fraction in SRF samples

Figure 5-43 illustrates the TG-DTG thermograms of commercially produced SRF samples obtained for model testing. The first two samples (SRF1 and SRF 2), that derived from the same MT/MBT plant and collected at the same period, present a similar thermal behaviour indicating the effectiveness of mechanical processing in the plant to produce relatively homogeneous samples and therefore with similar thermal behaviour: first DTG peak fluctuates between 3.7-3.8% w/w min⁻¹ in a temperature range of 334-339 °C indicating biomass degradation; second DTG peak between 7.1-7.4% w/w min⁻¹ in a temperature range of 470-474 °C indicating plastic degradation. Similarly, TG-DTG thermograms of SRF3 and SRF4 derived from the second MT/MBT plant at the same period are alike: first DTG peak ranges between 4.4-5.0% w/w min⁻¹ in a temperature range of 307-318 °C; second DTG peak between 4.8-5.0% w/w min⁻¹ in a temperature range of 470-472 °C. **Figure 5-43** shows that the samples from the first MT/MBT plant (SRF1 and SRF 2) contain higher plastic fraction than the samples of the second plant (SRF3 and SRF4) since second DTG peaks are higher, therefore the

biomass fraction is higher for the samples of the second plant. This is confirmed also by both model prediction (Table 5-21) and manual sorting (Table 4-13).

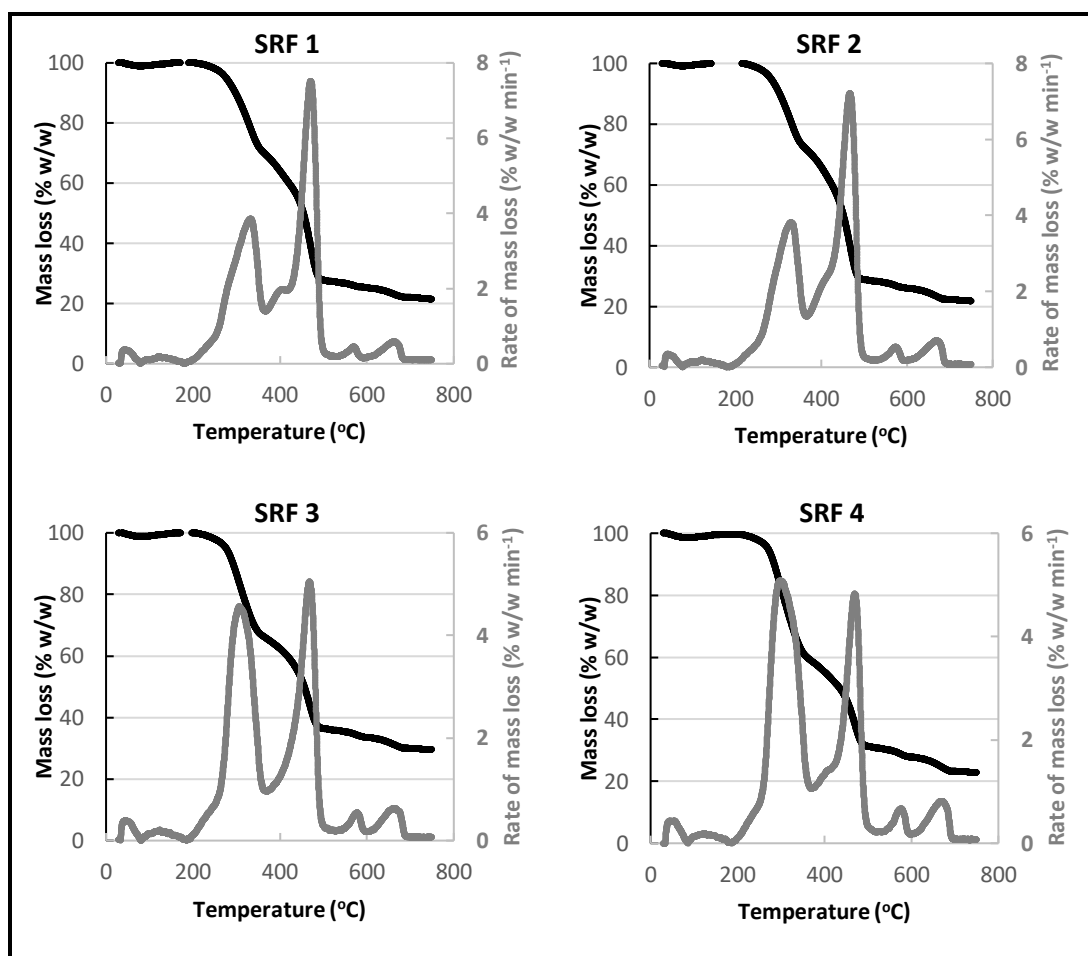


Figure 5-43. TG-DTG thermograms of commercially produced SRF samples in MT/MBT plants in the UK under *non-isothermal* operating conditions (atmosphere: nitrogen; flow rate: 50 ml min⁻¹; heating rate: 10 °C min⁻¹; sample holder: alumina 150 µl; sample mass: 10mg; maximum temperature: 750 °C) obtained from three replicate measurements.

Figure 5-44 visualises overlapping effects among prevalent SRF polymers considering the literature evidence (Section 2.4.2). For example, under the most prevalent TGA operating conditions (**Figure 5-6**) prevalent SRF polymers overlap in the following combinations: cellulose-hemicellulose, PE-PP, PET-polyolefins, while PVC and lignin overlap with all others. Therefore, biomass and fossil-based fraction overlap in TG-DTG experiments resulting in a biased estimation of SRF composition at this level (**Figure 5-44**).

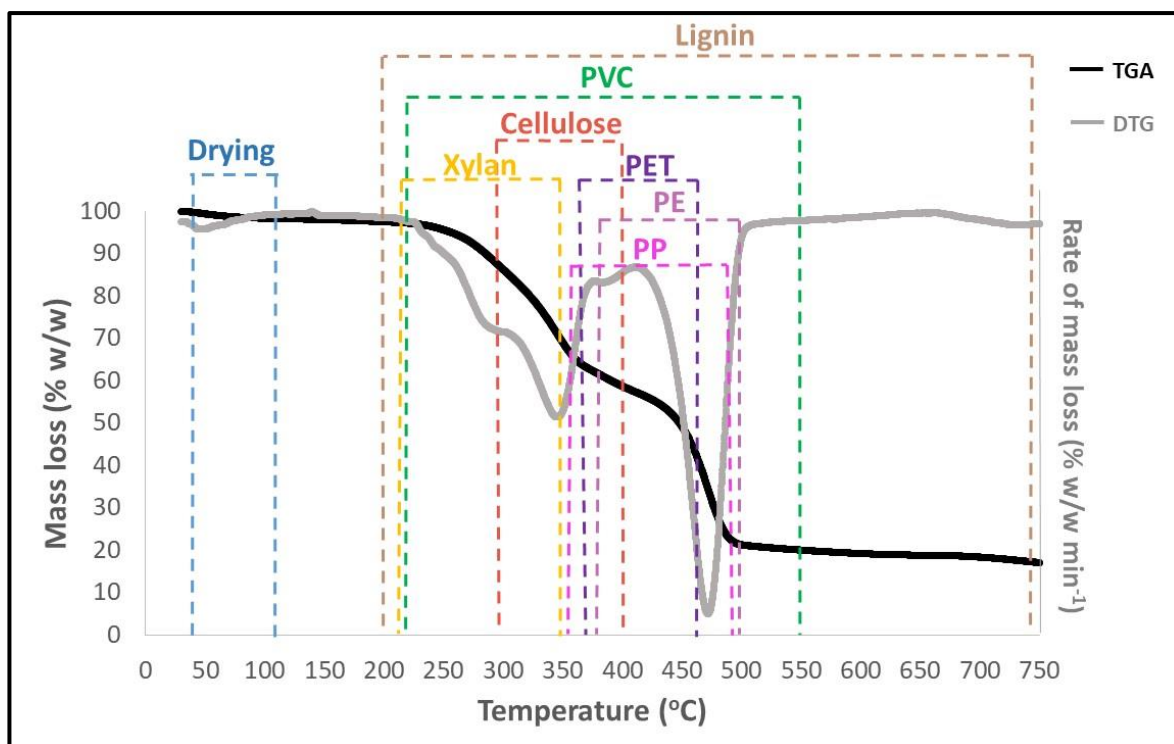


Figure 5-44. Typical TG-DTG thermogram of SRF/RDF based on the most prevalent component polymers: cellulose, lignin, xylan, PE, PP, PET and PVC (represents the Cl content) including water under inert atmosphere and low heating rate ($10\text{ }^{\circ}\text{C min}^{-1}$) as received reporting basis. (Axis of DTG curve was omitted due to unit inconsistencies among different studies leading to inability to obtain related information).

Table 5-22 shows the biomass and plastic fraction of SRF samples determined by three different ways: TG-DTG thermogram; manual sorting; and ML model.

Table 5-22. Biomass and plastic fraction (% w/w) of four commercially produced SRF samples used for model testing as determined by TG-DTG, manual sorting and ML prediction.

Method	Biomass fraction (% w/w)			Plastic fraction (% w/w)			Total (% w/w)		
	TG-DTG	Manual sorting	ML model	TG-DTG	Manual sorting	ML model	TG-DTG	Manual sorting	ML model
SRF1	35.67	42.62	54.32	39.02	33.41	45.68	74.69	76.03	100
SRF2	34.16	41.56	52.04	40.03	35.03	47.96	74.19	76.59	100
SRF3	34.30	49.41	55.30	30.40	31.66	44.70	64.70	81.07	100
SRF4	44.27	50.83	59.71	27.55	27.99	40.29	71.82	78.82	100

5.7.9 Precision of analytical measurements in TGA, DTG, and FTIR: $\text{RSD}_{\text{pooled}}$

Table 5-23 presents the precision of analytical measurements of synthetic mixtures (training and cross-validation set), waste mixtures (hold-out validation) and commercially SRF samples (testing)

for the obtainment of TGA, DTG, and FTIR datasets used for ML model development. The overall precision of all analytical techniques fluctuate at satisfactory ($> 16\%$) and similar levels for the three types of datasets. The highest analytical precision was obtained by FTIR (93.2-98.6%), followed by TGA (89.6-91.1%) and DTG (84.3 – 89.3%). The RSD_{pooled} of TGA and DTG indicate that precision of TG-DTG technique has a range of 86.7-92.8%. In the case of TG-DTG, the precision is lower for the training set (86.7%) than this of hold-out and testing set (90.2-92.8%).

Table 5-23. Overall precision analysis through TG-DTG and FTIR for the obtainment of three datasets – TGA, DTG, and FTIR – calculated by RSD_{pooled} (%) of the replicate measurements of synthetic mixtures (training and cross-validation set), waste mixtures (hold-out validation) and commercially SRF samples (testing) used for ML model development.

Analytical technique	Precision (%)		
	Training & Cross-validation	Hold-out validation	Testing
TGA	89.6	99.0	91.1
DTG	84.3	86.1	89.3
TG-DTG*	86.7	92.8	90.2
FTIR	98.6	98.1	93.2
DTG-FTIR*	91.7	92.3	91.3

*Derived from the RSD_{pooled} of TG-DTG and DTG-FTIR, respectively

6 DISCUSSION

This chapter presents the discussion of the results addressing their importance along with their relevance to previous research. The structure of this chapter is based on the chapter of the results (**Chapter 5**) and therefore these sections follow the sections of the results in a similar order.

6.1 Critical review discussion: risk of bias

In this section, a discussion on evidence obtained from the critical review analysis assessing the risk of bias is presented in three sub-sections following the results: i) Cl content in SRF co-combusted in cement kilns addressing the first research objective (**Section 5.1**); ii) typical content of SRF prevalent polymers in waste MCP categories (**Section 5.2**); and iii) most common operating conditions applied in TGA experiments of waste-derived materials (**Section 5.3**).

Critical review analysis entails bias which mainly occurs in the stage of selection process rather than in the stage of meta-analysis (Dwan et al., 2013). By following the PRISMA methodological approach, it is more likely to improve the reporting quality of systematic review and a better understanding of the selection process can be achieved resulting in bias minimisation (Knobloch et al., 2011). Herein, eligibility criteria related mainly to the examination of bias (e.g. insufficient or no inclusion of sampling process) were posed whenever was possible as several limitations were present. For example, the eligibility criterion in relation to the exclusion of studies with insufficient/ missing sampling process (**Figure 4-2**) refers to the compliance of studies with national or CEN/TC 343 standards. However, the rationale for estimation of the sampling process cannot be obtained without the inclusion of uncertainty along with analytical measurements (Ramsey, 2002), which was totally absent. In addition, some critical aspects such as the fate of Cl during SRF co-combustion in cement kilns were absent of literature evidence. Despite the careful assessment during publication selection, along with the evaluation of the results some aspects that may introduce bias are discussed in the following sub-sections.

6.1.1 Challenges around Cl at the stage of pre- and co-processing of SRF in cement kilns

At the stage of SRF pre-processing, the variability of Cl in SRF samples is a major challenge for wider uptake of SRF in cement kilns (Hinkel et al., 2019). The variability of [Cl] was high for both waste mixtures, MSW (**Table 5-1**) and SRF (**Table 5-2**), and waste component categories (**Table 5-3**) due to uncontrolled factors, such as seasonality and origin (Beckmann et al., 2012), partly unavoidable factors such as cross-contamination (**Section 2.4.3.1**) and controlled factors such as sampling (**Section 2.5.1.1**) and analytical methods (**Section 2.5.2.2**). This underpins the importance of research to quantify the opportunities for manipulating the controlled factors to further reduce the variability of Cl in SRF. From the waste component categories (**Table 5-3**), *plastics* had the highest Total [Cl] followed by *textiles*, *wood* and *paper/cardboard* indicating that the last two waste categories can be used to lower the SRF Total [Cl] (Velis et al., 2010).

Despite the similar levels of Total [Cl] between SRF (**Table 5-2**) and MSW (**Table 5-1**), the lower relative variation in SRF (36.7%) compared to MSW (52.8%) indicated the effectiveness of sorting and shredding unit operations employed in MT/MBT plants on SRF homogenization. It has been argued that the wide range of Total [Cl] in SRF (**Table 5-2**) can be largely attributed to the heterogeneity of solid waste depending on its composition. Deans et al. (2016) modelled the extent of uncertainty of [Cl] in SRF based on three different scenarios, depending on material composition, generating probability distributions using Monte Carlo simulations. They showed a greater spread of [Cl] in the case of SRF with high content in plastics (Deans et al., 2016).

Chlorine-related problems during SRF pre-processing can be controlled, and a number of options are available (**Table 2-10**). Yet, SRF producers need to consider that Cl content in SRF is widely dispersed amongst various items present in MSW, and is present in many chemical forms due to their wide application in packaging, textile and food industry materials (**Table 2-9**). This indicated the differentiation of sorting strategies during mechanical processing of MSW to produce an SRF which is low in Cl, going beyond the current preoccupation with identifying and/or removing only PVC.

However, the relative variation of [Cl] was higher for waste component categories than SRF (**Figure 5-1**). This was unexpected as SRF is a mixture of waste components while waste fractions have more uniform constitution. It is hypothesized that the higher relative variability of [Cl] in waste component categories (CV: 51.6-64.8%) is attributed to the different sorting rules and name definitions applied by researchers during characterization of waste fractions. For example, *plastics* is a generic waste component category that was arbitrarily divided into sub-groups (**Table 5-4**) such as *packaging* and *non-packaging* (Rotter et al., 2004) or *hard* and *soft* plastics (Ma et al., 2010; Nasrullah et al., 2016) increasing the risk of bias introduction due to e.g. limited precision of scale (HealthKnowledge, 2019), mass loss during sorting, and/or other practices related to human intervention (Gerlach and Nocerino, 2003). In addition to this, Sørum and Task (2001) reported that [Cl] may vary in some waste components depending on their physical properties or production methods. For example, [Cl] in paper depends on the bleaching process used for the removal of lignin (Bajpai, 2014), and [Cl] in plastics varies according to the polymer type (Heikkinen et al., 2004).

In contrast, SRF statistically analysed here was the outcome of commercial processes without any artificial sorting during the analysis stage. In addition, manual sorting of waste mixtures into specific waste component categories leads to an inevitable introduction of uncertainty due to grouping of heterogeneous materials into a notable waste component category with unpredicted and difficult to be accurately determined category, the *fines* (Séverin et al., 2010). The waste component category of *fines* might contain a significant and variable amount of another waste component category, e.g. plastic or organic fragments (Di Maria et al., 2013). Séverin et al. (2010) suggested to keep the number of waste component categories as low as possible during manual sorting of SRF samples.

In the stage of co-processing, **Figure 5-2** can be used as a theoretical framework by end-users and researchers for better understanding of the fate of Cl during SRF co-combustion in cement modern kilns. By combining this framework along with literature evidence on prevalent sources of Cl in SRF and related Cl-implications during co-combustion (**Section 2.4.3.2**), an overview of the impact of Cl on SRF marketability under current situation was given (**Figure 5-3**). This work is able to advise SRF end-users (cement kilns) to take decisions on Cl mitigation problems such as installation of bypass

system, and adjusting properly substitution rates and operating conditions (**Table 2-10**), but also to facilitate a better communication between end-users and producers leading to an efficient SRF trading (Velis et al., 2010). Understanding and therefore controlling the Cl variability by producers can lead to a more predictable and therefore manageable Cl distribution during co-combustion increasing market confidence in MT/MBT plants.

Despite Cl being considered the main technical limiting factor for SRF application in the cement industry (Cuperus, 2011; Lechtenberg and Diller, 2012; Pomberger and Sarc, 2014), critical review analysis confirms that the fate and related implications of Cl have not been rigorously studied. Most of the evidence exists for cases of high-Cl streams and not for MSW-derived SRF (e.g. hazardous waste or highly chlorinated substances present in the raw meal). Following this mass flow framework, most of Cl remains in the kiln (60-73%) indicating the higher risk of operating problems compared to stack emissions and clinker degradation quality (**Figure 5-2**). Cl circulation may affect the clinker manufacturing process and cause operating problems in the kiln, such as build-up and ring formation, corrosion and clinker quality degradation (**Section 2.4.3.2**).

The only recent study investigating the fate of Cl during co-combustion of SRF in modern cement kilns, i.e. with a preheater/precalciner system, was by Zhan et al. (2016). The effects of the bypass system on Cl circulation in modern kilns were examined by calculating the Cl balance. SRF was fed into the precalciner under a 6.5% mass substitution rate. The results showed that the absence of a bypass system induced 12.7% and 14.6% of input Cl to flow out through the clinker and flue gas respectively, while the remaining 72.7% remained in the inner surface of the preheater or accumulated in the cement ash. The presence of a bypass system with a bypass ratio close to 2%, led to 11.8%, 10.9% and 17.3% of the Cl input in the flue gas, the clinker and the bypass dust respectively, while 60% was the difference between input and output Cl.

However, literature evidence indicated that the way of feeding SRF into the kiln has a direct effect on the resulting emissions and therefore should be extensively investigated (Sarc et al., 2014). Sarc et al. (2014) is the only study that characterised and discussed the production requirements for SRF samples with different qualities that were fed into two a cement kiln via two different feeding ports: a high

SRF quality via the main burner; and lower SRF quality via the precombustion chamber. But, the fate of Cl in SRF has not been examined at all. Further investigation into the impact of feeding point is required to obtain a deep understanding on the fate of Cl during SRF co-combustion in cement kilns and the resultant implications (**Figure 5-3**).

6.1.2 Typical content of prevalent SRF polymers in main waste categories

Critical review analysis showed that the typical content of biopolymers varied to a different extent in several biomass waste component categories (**Figure 5-4**). The wider variation of biopolymers in *paper/cardboard* and *natural fibers* compared to *wood* waste category is attributed to the dependance of the content of biopolymers not only on the fiber type such as *wood*, but also on the pulping process (Liu et al., 2018). Cellulose clearly constitutes the most prevalent biopolymer in all categories, but in *paper/cardboard* and *natural fibers* it is considerably higher compared to *wood* and *non-wood biomass* (Watkins et al., 2015) due to the delignification process in papermaking (Viikari et al., 2009) and the need of textile industry to use fibers with high absorbency and whiteness (Jia et al., 2018), respectively.

Remarkably, the biomass waste category *non-wood biomass* could be incorporated into the category of *paper/cardboard* since it is mainly used for papermaking. However, this incorporation would require an accurate weight percentage participation of such materials in papermaking, otherwise a bias would be introduced in the quantification of biopolymers in *paper/cardboard*. There is evidence that *non-wood biomass* covers only 3% w/w of global pulp consumption with straw being the most prevalent *non-wood biomass* material, but it is a main source for areas where forest resources are scarce (Liu et al., 2018). Therefore, this percentage might be smaller or even trivial in Europe, the leading end-user of SRF. In Europe, hardwood fibers from oak, beech, poplar, birch and eucalyptus and softwood fibers from pine and spruce are mainly used in the papermaking industry (Cepi, 2020). Despite biopolymers, the percentage participation of fossil-based polymers in plastic fraction of SRF was indirectly estimated by studies that quantified their content in several stages of the supply chain (**Table 5-6**). However, these ranges might differ from the actual ranges of fossil-based polymers

content in SRF/RDF depending on the particular sub-fractions of MSW from which SRF/RDF are generated (e.g. household vs. commercial and industrial waste) (Nasrullah et al., 2015; Nasrullah et al., 2014), the targeted properties for SRF/RDF, e.g. maximum tolerant level of Cl (DEFRA, 2014), and the recovery efficiency of both MT/MBT plants (Velis et al., 2010) and material recovery facilities (Iacovidou et al., 2017b; Cimpan et al., 2016). For example, despite research and development efforts that have been conducted for the separation of black and highly coloured plastic materials from post-consumer plastic streams (e.g. via colour line camera (Neidel and Jakobsen, 2013), it still remains a challenge for material recovery facilities leading to the inclusion of these materials to the residual waste stream (Hinkel et al., 2019; Forrest, 2016).

6.1.3 Identification of TGA operating conditions for compositional analysis of waste materials

At this stage of critical review, the scope was to include TGA operating conditions from every publishable research focusing on compositional analysis of waste-derived materials and not only (Table 5-7), so that to obtain representative insights into the most prevalent operating conditions that would be selected in TG-DTG for the ML model development. Figure 5-6 revealed that the majority of TGA experiments of waste-derived materials were conducted under moderate conditions indicating the difficulty of researchers to deal with both complex SRF/RDF composition (heating rate ≤ 10 °C and inert atmosphere) and the maintenance of uniform thermal conditions throughout the TGA experiment (sample mass ≤ 10 mg). The preference of inert atmosphere is attributed to the fact that combustion is more rapid than pyrolysis and reactions between oxygen and waste components (e.g. lignin) might occur (Conesa and Rey, 2015; Long et al., 2017; Soares et al., 1995) making the compositional analysis of the sample more complicated.

However, many studies omitted to report the sample mass indicating that no special attention paid to this condition and therefore the inherent heterogeneity of solid waste might be underestimated. In addition, the inconsistency of units for the rate of weight loss in the literature did not allow to obtain comparable insights on the variability of thermal reactivity of commercial SRF/RDF samples.

Therefore, inert atmosphere, low heating rate (≤ 10 °C), sufficient temperature range for the material

degradation (maximum temperature ≥ 750 °C) and a representative amount of test portion depending on sample preparation can be recommended for TG-DTG compositional analysis of SRF/RDF.

6.2 Fitness-for-purpose sub-sampling plan for determination of SRF quality

In this section, a discussion on the results (**Section 5.4.3**) for establishment of an appropriate sub-sampling plan for SRF characterization (**O2**) is presented.

The selected sub-sampling plan can be considered a fitness-for-purpose for characterisation of SRF and other waste-derived materials with similar inherent heterogeneous composition. Noted that this sub-sampling plan can be used assuring representative results for determination of properties with variability that does not exceed the variability of Total [Cl]. Insights into the variability of SRF properties can be obtained by BS EN 15443 (2011) that provides data on the repeatability of measurements on SRF in the following order: copper (100%); nickel and cadmium (40%); antimony and mercury (30%); Cl, lead, chromium, cobalt, and vanadium (20%); arsenic (10%); NCV (4%); and dry matter (0.3%). Herein, it was ascertained that Total [Cl] was the most widely dispersed property compared to moisture, NCV, and ash (discussed onwards), but for other properties future research is needed to assess the risk of obtaining non-representative results. Even for SRF properties with higher variability than Cl, the established sub-sampling plan can be implemented obtaining two test sub-samples instead of one. Considering that the sub-sampling plan was established using state of the art equipment and the guiding principles of ToS following the general guidelines of CEN/TC 343 standards under the best combination time-cost-effort, the suggested sub-sampling plan is fitness-for-purpose and can be incorporated in related CEN/TC 343 standards (BS EN 15443, 2011; BS EN 15413, 2011) after the conduction of a Round Robin verification test.

The confidence intervals for binomial proportions were calculated with three methods (normal approximation, exact Clopper-Pearson and Wilson score method) to determine the possibility to obtain representative results by drawing either one (**Table 5-11**) or two test sub-samples (**Table 5-12**).

Table 5-11 indicated that the possibility to obtain a non-representative test sub-sample ($RSD > 15\%$) for the determination of Total [Cl] was not negligible (CI: 57-93% to be representative), while the obtainment of two test sub-samples (**Table 5-12**) significantly improved the possibility to obtain representative sub-samples (CI: 91-98%) increasing importantly the time and cost of the sub-sampling process. Despite the absence of research on quantification of sampling (and sub-sampling) uncertainty in solid waste characterisation, literature evidence indicated that an acceptable limit of uncertainty at 15% is quite difficult to be obtained in case of Total [Cl] determination. For example, Aldrian et al. (2016) reported that the relative standard deviation of Cl for two SRF laboratory samples derived from five test sub-samples ranged from 17.2% to 21.8% (Aldrian et al., 2016), although cryogenic shredding was not implemented in the stage of sample preparation. Therefore the interval of possibility to obtain representative analytical results of Total [Cl] following the established sub-sampling plan would be considerably higher if the acceptable level of uncertainty was higher. For example, if the uncertainty limit was 20%, there would be only one failure (4th test sub-sample) instead of three (**Table 5-10**).

In **Table 5-10**, the range of Total [Cl] in the 16 sub-samples (0.48% w/w_d) was comparable with the intervals between the class codes for the limit values of Cl content in SRF specified by CEN/TC 343 classification scheme (BS EN 15359, 2011). For example, the difference of Total [Cl] between class code 2 ($\leq 0.6\%$ w/w_d) and class code 3 ($\leq 1\%$ w/w_d) is 0.4% w/w_d which is lower than the range of Total [Cl] in the 16 test sub-samples (0.48% w/w_d), whereas the difference between class code 3 ($\leq 1\%$ w/w_d) and class code 4 ($\leq 1.5\%$ w/w_d) is slightly higher (0.5% w/w_d). The determination of Total [Cl] in the 16 sub-samples led to different classification results amongst the SRF sub-samples: 7 out of 16 sub-samples were designated as class code 3 and 9 out of 16 sub-samples were designated as class code 4 (**Figure 5-12**). The different classification amongst the 16 sub-samples was mainly due to the proximity of mean value (1.08% w/w_d) in the border between the class code 3 and class code 4 (1.0% w/w_d).

The construction of nomographs denoted the logarithmic increase of uncertainty as the sample mass decreased (**Figure 5-9**). For the scenarios with shredding (PS and CS), the 1st stage of riffle splitting

(from A to B) applied before primary shredding introduces the highest uncertainty (FE: 23.9%) compared to the next sub-sampling stages due to the largest particle size ($d \approx 3$ cm). This phenomenon indicated the urgent need for primary shredding, which drops the FE in the next stages of riffle splitting. If no primary shredding applied, which was the NS scenario (A-B-C), the uncertainty would be increased logarithmically during sub-sampling (overall FE: 1272.6%). The considerably lower uncertainty observed in the PS scenario (overall FE: 113.7%) indicated that primary shredding applied after the 1st stage of riffle splitting can reduce the overall FE more than 11 times. By comparing the PS with the CS scenario (overall FE: 33.6%), the overall FE decreased more than 3 times if the particle size of the test sub-sample drops from 0.4 cm to 0.015 cm with the use of CryoMill. The beneficial role of cryomill was also revealed by the contribution of the final stage of sub-sampling to the overall FE for the two scenarios: PS and CS. For the PS scenario, the FE arising from the final stage of sub-sampling (FE from E to F: 108.7%) contributed 96% to the overall FE, whereas the FE arising from the final stage for the CS scenario (FE from G to H: 0.9%) contributes less than 3% to the overall FE (**Appendix C3**). Note that these differences did not include any bias that might be induced by a larger particle size (e.g., insufficient CI recovery).

However, experimental results showed that the established sub-sampling plan can result in representative sub-samples (13 out of 16) with uncertainty less than 15%, whereas the maximum overestimation observed in the 4th test sub-sample (27.6%) did not exceed the theoretical ToS calculations (FE: 33.5%). These findings support the need for exploring the applicability of the ToS-based formula to the determination of analytes with considerably variable concentrations amongst the particles/components of waste-derived materials (**Section 6.3.1**).

The implementation of cryogenic shredding found to be an important and necessary sample preparation process to the establishment of an appropriate sub-sampling protocol for characterisation of the highly inherent heterogeneous SRF (**Figure 5-9**). However, **Figure 5-8** showed that configuration settings of cryomill did not considerably affect the sub-sampling uncertainty. From the statistical point of view, the PSD was significantly different amongst the shredding programs. However, this difference (μm -scale) was negligible compared to the difference (cm-scale) between

the particle size before (3 cm) and after (0.4 cm) primary shredding. The FE of the final sub-sampling stage was considerably lower than the FE of previous stages, where the particle size was one order of magnitude greater. In the most extended shredding program (P9) the FE arising from the final stage (0.3%) constituted less than 1% of the overall FE (33.6%). Even in the least extended program (P2), the FE of the final stage was less than 10% of the overall FE. This finding enabled the selection of an affordable and less time-consuming operation setting of cryogenic shredding without considerably increasing the sub-sampling uncertainty. However, in the characterisation of SRF properties with potentially higher variability than this of Total [Cl] such as PTEs (BS EN 15443, 2011), the configuration settings might have a more considerable impact. The beneficial role of cryogenic shredding in sample preparation has also been discussed by Junghare et al. (2017) reporting that cryogenic shredding prevented component evaporation, oxidation and/or microbial degradation due to the integrated cooling system earning interest on sample preparation of solid waste (Junghare et al., 2017).

Monitoring of incorrect sub-sampling practices showed that shredding did not significantly affect the MC (**Figure 5-10**) and therefore the determination of SRF properties expressed on dry basis did not contain any significant systematic error. However, the situation might be totally different in determination of other analytes, more volatile than MC. Specifically, the evaporation of mercury, the key environmental performance attribute (BS EN 15359, 2011), during shredding is of concern and special attention should be paid (Gerlach and Nocerino, 2003).

By tracking the loss of mass during mass reduction and shredding processes (**Figure 5-11**), it was realised that mass loss cannot be zero, even under careful sub-sampling practices conducted by a well-trained operator. It should be noted that riffle splitters are composite sub-sampling devices with high performance depending on the training skills of operator and the fraction of fines in the sample (Dominy et al., 2018a). A considerable mass loss of sample during sub-sampling results in the loss or gain of analyte depending on the location of its particles, whether they are included in the lost mass or not (Gerlach and Nocerino, 2003). Although the mass loss of 0.7% w/w during sub-sampling indicated that 5.97 g out of 851.31 g of total sample mass had zero probability to be included in the

test portion for analysis (**Figure 5-11**) introducing bias based on ToS, this amount can be considered negligible (Edjabou et al., 2015).

The last incorrect sub-sampling practice that was examined was the recovery of Total [Cl] (**Table 5-9**) indicating that even cryogenic shredding of synthetic mixtures did not reach 100% *R* of Total [Cl]. Cuperus et al. (2005) estimated the *R* of the Total [Cl] in SRF by means of BC combined with IC, reporting that *R* can reach up to 100% when the particle size of the test portion is < 5 mm. Here, the size was lower (0.15 mm), but *R* was not 100%. Hence, the reason might be the loss of Cl during the bomb ventilation. Ma et al. (2010) reported that BC measures 15-25% less Total [Cl] compared to other analytical methods due to potential incomplete combustion in the bomb or Cl loss during bomb ventilation.

6.3 Sub-sampling uncertainty for determination of SRF quality

In this section, a discussion on the uncertainty arising from sub-sampling for SRF characterization (**O3**) is presented in three parts following the results, as far as possible: i) comparison of empirical approach (DoE1: nested design) versus ToS-formula (**Section 5.5.2** and **Section 5.5.3**); ii) uncertainty for determination of classification SRF properties (moisture, ash, Cl, and calorific content) (**Section 5.5.1- Section 5.5.3**); and iii) uncertainty for determination of combustion behaviour of SRF with the use of TG-DTG (**Section 5.6**).

6.3.1 Nested design versus ToS

The results have shown the merits and demerits of both approaches applied for the quantification of sub-sampling uncertainty, ToS and nested design (**Section 5.5.2**). The ToS formula considered the physical and chemical characteristics of the sample as constant factors into the equation, but these factors might be considerably different between sub-samples depending on the size and composition of every particle contained in the sub-samples (Francois-Bongarcon and Gy, 2002). For example, particles with variable sizes in the sample may have a different chemical composition or particles with different composition may belong to a specific particle size and/or the analyte might be abundant in

some particles and confined in others (Ramsey and Thompson, 2007). Thus, the target material tends to behave more unpredictably rather than predictably as ToS implies (Ramsey and Thompson, 2007).

This behaviour was observed by the results of nested design (**Figure 5-15** and **Figure 5-16**). The RSD for MC was slightly increased as the sub-sample mass reduced in *Gross_nested* design, but the reverse behaviour observed from the 5th to the 7th stage in *Intra_nested* (**Figure 5-15-A**). This trend was also observed for the determination of NCV, the RSD arising from the 6th stage (0.2%) was 3 times lower compared to the 5th stage (0.6%) (**Figure 5-15-A**). In addition to this, the relative contribution of the sub-sampling stages to the overall uncertainty was different for each SRF property despite the identical sub-sampling process applied in SRF properties (**Figure 5-16**). Unless the target material has a predictable physical and chemical constitution, such as a narrow range of particle size and uniform dispersion of analyte into the sample, ToS formula can be inaccurate (Ramsey and Thompson, 2007; Francois-Bongarcon and Gy, 2002). Besides, the effort needed to accurately quantify the determinants of sampling factor (**Eq. 2-4**) would exceed the effort to quantify empirically the sampling uncertainty due to the significant amount of information required for the target material (Ramsey and Thompson, 2007).

The results of nested design revealed the lower sensitivity of a balanced nested design to detect the variance at upper levels, where the degrees of freedom were fewer (**Table 5-16**). The number of pairwise comparisons between sub-samples nested within the sample was larger in the last stages than in the first stages increasing the sensitivity to reject the null hypothesis. For example, the null hypothesis at the 5th stage, which was the first stage of *Intra_nested* design, considered that the mean value of analyte in sub-sample *a* was equal with that in sub-sample *b*. Still, the null hypothesis at the 7th stage (or final stage of *Intra_nested* design) was that: the mean value in sub-sample *a11* was equal with the mean value in sub-sample *a12*; and *a21* equal with *a22*; and *b11* equal with *b12*; and *b21* equal with *b22* (**Figure 4-5**). RSD for the 4th stage was higher than the 5th stage for most SRF properties (except to MC), which was opposed to the tendency of uncertainty to be increased as the sample mass is reduced (**Figure 5-15**). This was attributed to the breakdown of nested design in *Gross_nested* (1st – 4th stage) and *Intra_nested* (5th – 7th stage). From the statistical point of view,

balanced nested designs have higher statistical power to the later levels than preceding levels due to more *d.f.* (Ojima, 2000). The 5th stage which corresponded to the first level of *Intra_nested* had only one degrees of freedom, whereas the 4th stage which corresponded to the final stage of *Gross_nested* had eight degrees of freedom.

But, the construction of an unbalanced nested design in order to create a better balance of *d.f.* amongst the stages would reduce the power of ANOVA test (Shaw and Mitchell-Olds, 1993). Balanced nested designs are orthogonal and the estimators of the variance components are independent resulting in higher precision of estimates than unbalanced designs, which are more sensitive to the assumptions of homoscedasticity and normality (Fernandes et al., 2012; Schielzeth and Nakagawa, 2013). Unless the entire sample mass is analysed, we cannot quantify accurately and precisely the sub-sampling uncertainty. Here, the variance components derived from 72 analytical measurements (48 in *Gross_nested* and 24 in *Intra_nested* design). In the case of NCV and Total [Cl], this amount of measurements included the analytical determination of 2.5% w/w of total sample mass (test portion 0.3 g x 72 measurements = 21.6 g out of 850 g) and in the case of MC and Ash this percentage was 8.5% w/w (test portion 1 g x 72 measurements = 72 g out of 850 g). However, a prudent use of ANOVA under a strict sub-sampling protocol can give valuable results (Flamme and Geiping, 2014; Analytical Methods Committee, 2012). The prerequisites for using ANOVA were thoroughly checked (**Appendix D3**), experiment randomization was applied and advanced sub-sampling practices and equipment following the established sub-sampling plan were used in order to produce trustworthy results (Gerlach and Nocerino, 2003; Montgomery, 2017).

Despite the lower sensitivity of nested-ANOVA to detect variance in upper levels, the comparison of RSD between the sub-sampling stages with equal degrees of freedom (e.g. 1st with 5th, 2nd with 6th, and 3rd to 7th) demonstrated the upward trend of RSD as the sample mass decreases. An exception was observed in the case of NCV as the RSD introduced during the 1st stage (1.4%) was more than twice higher than the 5th stage (0.6%).

Both approaches, nested design and ToS, were in agreement regarding the dependence of sub-sampling uncertainty on SRF property (**Figure 5-13**). Based on ToS, the lower the concentration of

analyte, the higher the sampling uncertainty (Pitard, 1993). The highest uncertainty was introduced for the determination of Total [Cl] due to its lower fraction in the sample (average 1.09% w/w_d) compared to the other SRF properties, whereas the lowest uncertainty found in MC determination (average 16.62% w/w).

However, the ToS approach gave a substantially higher overall sub-sampling uncertainty than nested design (**Figure 5-13**). For example, RSD estimated by ToS was more than 3 times higher compared to nested design for the determination of MC (2.6%) and Ash (6.1%). This difference was less than twice for Total [Cl] as the RSD was statistically determined at 18.2% and theoretically estimated at 31.3%. The statistical approach was expected to give higher RSD than the theoretical since ToS-based formula calculated the RSD only due to constitutional heterogeneity of the material (FE), whereas the RSD from nested-ANOVA included all the related factors that may introduce uncertainty, such as sample preparation, experimenter skills, performance of sub-sampling methods and analytical errors.

One reason for this difference (nested design vs ToS) could be related to the inability to obtain precise quantification of RSD based on ToS due to insufficient amount of information required for the precise calculation of sampling constant, *C* (**Section 4.2.3**). But, differences were also found between their relative contributions (**Figure 5-16**). ToS approach gave a substantially higher relative contribution in the sub-sampling stages (**Figure 5-16**), where either the particle size was large (1st stage) or the test sub-samples were not cryogenically shredded (AE stage for MC and Ash).

In the stage of AE (from test sub-sample to test portion), ToS found that the RSD for MC and Ash was more than 10 times higher in comparison with the nested design (**Figure 5-15**). At this stage of nested design, the degrees of freedom of nested design were sufficient in order to concern about the statistical power of the design. Furthermore, from the perspective of ToS, the sampling constant, *C*, did not change in the final stages (no shredding) for MC and Ash, whilst the difference between the two approaches became considerably wider compared to the previous stage (7th). Thus, the high difference between the two approaches in the AE stage for MC and Ash was not related neither to the lower sensitivity of balanced nested design in the upper stages nor to the inaccurate calculation of sampling constant. The role of particle size in the sub-sampling uncertainty seemed less important

than ToS formula performs. This was also confirmed by the fact that only for Total [Cl] the RSD arising from the AE stage, where cryogenic shredding was applied, calculated by nested design was more than 6 times higher than the RSD based on ToS. It was the only stage (AE), in which the theoretically estimated RSD (ToS) was considerably lower than the statistically calculated (nested design).

These findings indicated that the particle size of the sample might affect less the sub-sampling uncertainty than ToS stipulates. However, the 2nd stage, in which sub-samples had the highest sub-sample mass (circa 450 g) with the lowest particle size (< 0.4 cm) compared to the other sub-sampling stages (**Table 5-15**), provided the lowest relative contribution for all SRF properties based on both approaches (**Figure 5-15**). Most of the particles in solid waste tend to be either flat (i.e. paper and textiles) or hollow (e.g. containers), thus their thickness does not change with shredding so much as in granular materials, in which ToS is mainly applied. ToS-based formula needs revaluation and possibly adjustment regarding the proportional relationship between FE and the cube of particle size ($d^3 \propto FE$) before applied in the sub-sampling for waste-derived materials. Nevertheless, the role of ToS is to provide guidance on correct sampling practices and equipment so that to adopt a sampling plan able to minimize the uncertainty (Gerlach and Nocerino, 2003; Ramsey and Thompson, 2007).

6.3.2 Uncertainty for Moisture, ash, NCV and Total [Cl]

DoE1 was a novel approach able to estimate the variability in critical properties for SRF quality and therefore highlight the need to estimate the uncertainty in SRF QA. However, the limited attention to this aspect by waste processing sector (Esbensen and Velis, 2016) makes difficult to obtain any comparative observation. The only related research found was by Cuperus et al. (2005) that quantified the performance of sample preparation on determination of SRF properties including PTEs and Total [Cl]. The performance of sample preparation mainly attributed to shredding was tested by measuring the repeatability and recoverability through an indirect experimental method under two particle sizes: 1mm and 0.5 mm. Specifically, two series of 10 duplicate SRF sub-samples for each particle size subjected to chemical analysis. In the first series, the preparation of duplicate sub-samples was identical considering that represents the uncertainty only due to analysis, while in the second series

the preparation of duplicate sub-samples was individual including both uncertainty due to analysis and preparation (Cuperus et al., 2005). It was considered that the duplicate sub-samples had identical compositions, as they were drawn simultaneously from the same source. Results showed that the analysis of sub-samples with particle size 1mm for characterization of Total [Cl] had an uncertainty 17% due to analysis and 31% due to preparation, while for a particle size 0.5 mm the uncertainty was 18% due to analysis and only 1% due to preparation (Cuperus et al., 2005).

Herein, the uncertainty was quantified at each stage of sub-sampling considering conjointly constitutional heterogeneity, sample preparation, and mass reduction making difficult to compare the uncertainty of sample preparation with this of Cuperus et al. (2005). By comparing the uncertainty of analysis (AE), Cuperus et al. (2005) found a considerably larger uncertainty (17-18%) than in the present uncertainty (AE: 5%) (**Table 5-17**). This difference between the present study and Cuperus et al. (2005) might be attributed to the considerably lower particle size of test sub-samples (0.15mm vs 0.5mm), the different analytical method (Palintest Chloridol test vs IC), and/or other factors that may introduce bias in the calculation of uncertainty (**Section 4.2.5**). Yet, the RSD remained constant in the 2nd sub-sampling stage (2.2%) with this of the 1st sub-sample stage (2.3%) while the sample mass decreased 50% (**Table 5-17**) due to particle size reduction at 0.4 cm indicating the beneficial role of Cutting Mill in the reduction of the uncertainty. This finding is in agreement with Cuperus et al. (2005) regarding the uncertainty of sample preparation.

The RSD arising from the AE stage which described the variability of replicates ranged at acceptable levels (< 5%) being only a small part of the overall sub-sampling uncertainty (7.1-12.9% of total RSD) for the selected SRF properties (**Figure 5-16**). By considering also the bias related to the recovery of Total [Cl] during BC (**Table 5-9**) which was calculated at ca. 98.3% (bias: 1.7%), the greatest part of AE for Total [Cl] determination (AE: 5%) emerged from sub-sampling (from test sub-sample to test portion) rather than analysis. These findings confirms the statement that the sub-sampling uncertainty may considerably exceeds the analytical error in highly heterogeneous materials (Gerlach and Nocerino, 2003) (**Table 5-17**). The properties of solid waste need to be specified by a level of uncertainty using: quality control practices, such as reference materials for the calculation of

systematic errors (Prichard and Barwick, 2007), replicate measurements (Prichard and Barwick, 2007), randomization (Montgomery, 2017), correct sampling practices and equipment (Gerlach and Nocerino, 2003); and statistical tools (Esbensen and Velis, 2016) (Velis et al., 2010).

Based on the results of nested design, the overall uncertainty for the determination of relatively uniformly dispersed analytes in solid waste (**Figure 5-13**), such as MC, Ash and NCV can be considered acceptable ($RSD \leq 6.1\%$). However, the uncertainty for the less uniformly dispersed Total [Cl] ($RSD: 18.2\%$) exceeded the 15% reference limit. Chlorine in SRF varied widely between SRF components (**Table 2-9**) and its variability has preoccupied researchers more than any other SRF property (Deans et al., 2016; Ma et al., 2010). For example, specific plastic polymers, such as PVC and PVdC are highly chlorinated materials with Total [Cl] ranging from 46 – 73%, whereas Cl is absent in PP and HDPE.

The analytical determination of analytes in SRF and generally in solid waste must include the sampling uncertainty (Flamme and Geiping, 2014; Ramsey, 2002) providing a probabilistic interpretation of the results (Ramsey, 2002). Specifically, compliance evaluation with existing quality management specifications requires the incorporation of the uncertainty level of the measurand at a selected set limit leading to the creation of acceptance and rejection zones (Velis, 2010). In most studies the properties of solid waste are expressed as individual values and the standard deviation of replicates might be given. However, the variability of replicates, known as repeatability, refers to the precision (closeness of measurements to each other) and not to the accuracy (proximity to the true value) of analytical results (Prichard and Barwick, 2007).

The uncertainty states the difference between the experimentally identified estimate (measured value) and the true value (also known as real population value). Here, RSD indicated that the Total [Cl] in a test sub-sample could be up to 0.20% w/w_d below or above the average Total [Cl] (1.09% w/w_d), which represented the true value, still an unknown quantity, in the SRF sample. Insights on the difference between the true value and the estimate of average of Total [Cl] derived from 17 sub-samples (16 in *Gross_nested* design and 1 in *Intra_nested*) were obtained by the margin of error, which was 0.08% w/w_d at 95% confidence level. Putting this into perspective, the overall RSD did not

exceed the intervals ranges used in the class codes of classification CEN/TC 343 SRF scheme (BS EN 15359, 2011), which can be from 0.4% w/w_d to 1.5% w/w_d (class code 1 $\leq$ 0.2% w/w_d; class code 2 $\leq$ 0.6% w/w_d; class code 3 $\leq$ 1% w/w_d; class code 4 $\leq$ 1.5% w/w_d; and, class code 5 $\leq$ 3% w/w_d).

The urgent need to customise a tolerable level of uncertainty of analytical measurements was also stressed by comparing the variability around the mean of Total [Cl] (36.7%) derived from several commercially produced SRF samples obtained from critical review analysis (**Table 5-2**) with the statistically calculated sub-sampling uncertainty (RSD of Total [Cl]: 18.2%). Since the sub-sampling uncertainty was considerable for determination of Total [Cl] in one SRF sample of ca. 1kg under a fitness-for-purpose sub-sampling plan (**Section 6.2**), the variability of Cl among different SRF samples from several regions was reasonably expected to be significantly higher due to different suppliers, mechanical processing, type of waste feedstock, and sampling and experimentation procedures. The inclusion of uncertainty around the arithmetic mean of Total [Cl] by reported studies would improve the reliability of the interpretation of Cl variability in SRF samples obtained in **Table 5-2**. This information would enable also to assess the performance of sampling protocols applied by researchers and therefore improve the performance of samplers (Ramsey, 2002).

Higher levels of uncertainty can in fact be tolerable and fit-for-purpose, depending on the user needs, inherent material heterogeneity and the variability of analyte in the sample (e.g uniformly dispersed analyte such as the chemical substance in a drug or less uniformly dispersed analyte such as PTEs in solid waste) (Ramsey and Thompson, 2007; Bethem et al., 2003), because representative sampling might be never fully achieved (Ramsey, 2002). Taking into account the highly inherent heterogeneous composition of SRF (**Table 2-3**) and the considerable Cl variability in waste component categories (**Table 5-3**), the sub-sampling plan able to obtain values that lied within a permissible range for the classification of SRF can fulfil the fitness-for-purpose requirements. Besides, end-users have to acknowledge that there is always the possibility of incorrect classification of SRF associated with Cl even under a thorough sub-sampling protocol, but this possibility can be confined and controlled with the use of appropriate practices and equipment. Arguably, lowering the sub-sampling uncertainty of the Cl with the current technological state of the art would possibly require excessive effort and cost.

However, in case of less uniformly dispersed hazardous properties (e.g PTEs) the analysis of duplicate samples for a single lot might be needed (BS EN 15443, 2011).

6.3.3 Uncertainty for thermal behaviour via TG-DTG

Following the established sub-sampling plan, the estimated level of overall uncertainty for TG-DTG of SRF (**Table 5-19**) remained considerable (RSD_{pooled} : 32.2%) indicating that the reference limit value ($\leq 15\%$) is difficult if not impossible to be reached. This would require excessive effort, time and cost which contradicts to the notion of fitness-for-purpose requirements. Besides, Ramsey (2002) stated that even a high level of 50% uncertainty can be fit for some specified purposes addressing that reliable estimates of uncertainty can lead to probabilistic interpretation of the results helping to define an acceptable level of uncertainty. In any case, SRF end-users should consider the high inherent material heterogeneity, the tiny required amount of test portion for TG-DTG, and affordable cost of the sub-sampling scheme.

The sub-sampling uncertainty for the characterisation of SRF combustion behaviour (**Table 5-19**) did not exceed the reference limit value ($\leq 15\%$), although the uncertainty for DTG points was higher (RSD_{pooled} : 7.2%) compared to TGA (RSD_{pooled} : 5.2%). DTG constitutes the derivative of TGA capturing more information and therefore more variance than TGA (Golan, 2018). The overall uncertainty of the entire TG-DTG signal (**Table 5-19**) was considerably higher (RSD_{pooled} : 32.2%) as critical combustion characteristics constituted only a small amount of entire TG-DTG signal (38 points out of 10,442). By comparing the uncertainties between critical points (**Table 5-18**) and entire TG-DTG signal (**Table 5-19**), it was revealed that the higher uncertainty in the latter was mainly due to DTG signal (RSD_{pooled} : 44%). For TGA, the uncertainty of critical points (RSD_{pooled} : 5.5%) was ca. 50% lower than this of the entire TGA signal (RSD_{pooled} : 11.6%), while for DTG the difference was ca. six fold (7.2% vs 44%). This observation indicated that the TGA critical points can sufficiently capture the variance of TGA signal, but the critical points of DTG were not able to sufficiently describe the DTG signal and consequently the thermal profile of the rate of weight loss.

There is a previous study that quantified the repeatability of TG-DTG results for RDF by calculating the RSD of several test sub-samples subjected to three different shredding procedures – knife milling, rotary grinding and cryogenic shredding – for determination of characteristic thermal degradation points (Robinson et al., 2016). This RSD for the cryogenically shredded test sub-samples reported by Robinson et al. (2016) can be compared with the AE of the critical combustion points (**Appendix E4: Table E5-2**). **Table 6-1** presents the AE for critical TG-DTG points as quantified by both Robinson et al. (2016) and the present study. Despite some differences between Robinson et al. (2016) and the present study regarding the TG-DTG operating conditions (heating rate: 25°C vs 10°C; and atmosphere: inert vs air), the test sub-sample mass (2.5 g vs 6.6 g), the number of replicates (15 vs 3) and the number of test sub-samples (3 vs 24), the results of this research were in high agreement with Robinson et al. (2016). Considering the relative contribution of AE (35.9%) to the overall RSD (**Table 5-18**) along with the comparative findings in **Table 6-1**, it is confirmed the effectiveness of cryogenic shredding in sample preparation of waste-derived materials for TG-DTG. Specifically, Robinson et al. (2016) stated that cryogenic shredding is the most suitable sample preparation procedure able to provide repeatable TG-DTG results due to considerably fine grinding and high material recovery.

Table 6-1. Comparative results between Robinson et al. (2016) and the present study on the AE of critical TG-DTG points for SRF/RDF applying cryogenic shredding to test sub-samples.

TG-DTG critical points	Variable ¹	Robinson et al. (2016)		Present study	
		Average	AE (%) ²	Average	AE (%)
Residual moisture (wt.%)	Var 6	2.38	2.9 – 35.4	2.57	4.8
Content of cellulosic volatiles (wt.%)	Var 9 & Var 12	48.04	0.3 – 1.1	51.02*	2.3**
Content of plastics (wt.%)	Var 15	28.01	0.6 – 1.4	30.01	2.0
Content of high-temperature volatiles (wt.%)	Var 18	4.36	1.0 – 18.0	3.08	4.1
Ash	Var 21	16.28	3.8 – 8.5	12.85	6.3

¹From **Table 4-5**; ²Derived from three RDF test sub-samples *Sum of mass loss at 1st_ML and 2nd_ML; **RSD_{pooled} of 1st_ML and 2nd_ML

Nested design showed that relatively representative results ($< 15\%$) can be obtained paying special attention to sub-sampling process (**Table 5-18**). From total 38 critical TG-DTG points used to estimate the sub-sampling uncertainty, only 3 points exceeded the reference limit value of 15% (**Figure 5-20**): the third DTG peak at 425.3°C (Var30) indicating the plastic degradation with the highest uncertainty (RSD: 21.5%) due to the fast thermal decomposition of plastics (Nisar et al., 2011) and higher inherent heterogeneity of plastic fraction compared to other waste component categories present in SRF (**section 2.4.1.2**); the combustibility index, S, (RSD: 19.4%) due to the propagation error derived from the uncertainty of each factor used for its calculation (**Eq. 4-3**); and the residue (Var21) that slightly exceeded the reference limit (RSD: 15.7%).

Interestingly, the sub-sampling uncertainty for residue determination using TG-DTG (RSD: 15.7%) was more than 2.5 times higher than this for determination of ash content (RSD: 6.1%) under identical riffle splitting and sample preparation procedures. This difference might be attributed to different amounts of test portion since the test portion for TG-DTG (10 mg) was ca. 100 times lower compared to this for ash determination (ca. 1 g) leading to higher uncertainty for determination of the residue content compared to ash as ToS stipulates (Gerlach and Nocerino, 2003). But, the relative contribution of AE to overall uncertainty in ash determination estimated at 7.9% (**Figure 5-16-B**), while for residue was at 20.8% (**Figure 5-20-E**). This comparison does not justify the high overall RSD difference between ash and residue, despite measurements derived from identical test sub-samples. It was estimated that SE was 14.4% for determination of Residue, still higher than the overall RSD for ash (6.1%). Therefore, the difference is also attributed to dynamic perturbations of TG-DTG. Contrarily to TG-DTG in which measurements are dependent on a dynamic thermal profile, analytical technique for ash content is static in nature providing more constant measurements (Adani et al., 2002) and therefore is preferred.

Despite the identical sub-sampling plan and analysis applied for the determination of several characteristic TG-DTG points, the relative contribution of SE and AE to overall RSD showed a wide variability amongst the critical points (**Figure 5-20**), which was in agreement with other SRF properties (**Section 6.3.2**). For the majority of variables, the main source of total RSD was SE with an

averaged relative contribution 64.1% (**Table 5-18**) stressing the special attention that should be paid to sample preparation and sub-sampling practices before TG-DTG. Only in 6 out of 38 combustion characteristic points including S, AE had greater contribution to total RSD than SE. Specifically, AE was higher than SE for determination of variables 33 (PC1), 19 (PC3), 7, 31, 35, and 37. However, total RSD for these variables was low ($< 6\%$) indicating no high concern.

In addition, the overall precision analysis of TG-DTG calculated by RSD_{pooled} of the replicate measurements of synthetic mixtures used for ML model training (**Table 5-23**) indicated that the AE was 13.3% (overall precision: 86.7%). This uncertainty was 35.1% lower compared to the AE of TG-DTG of a commercially produced SRF sample (20.5%) as calculated by nested design (**Table 5-19**). This is reasonable since waste samples are more heterogeneous than synthetic mixtures due to the involvement of a wider variety of materials and impurities. This comparison (**Table 5-23** vs **Table 5-19**) also indicated that the lower AE observed in the hold-out (waste mixtures: 7.2%) and testing sets (SRF samples: 9.8%) compared to training set (synthetic mixtures: 13.6%) was due to the higher sample population of the training set ($n=53$) compared with hold-out validation ($n=6$) and testing set ($n=4$) and therefore higher ability to detect variations in the training set. An increase of replicate measurements for TG-DTG of commercially produced SRF samples could improve the credibility of the level of precision (Prichard and Barwick, 2007).

For the TGA, the AE for the training set (10.4%) exceeded the AE of nested design (6.4%). This might be attributed to the different atmospheric TGA conditions (combustion vs pyrolysis) and/or the different time period (over a year) conducted the two DoEs during which the sensitivity of TGA apparatus might be changed. Combustion is more rapid than pyrolysis (Conesa and Rey, 2015; Long et al., 2017; Soares et al., 1995) making the TGA signal to capture less variation. However, in both atmospheres, AE for TGA can be considered relatively low indicating the effectiveness of cryogenic shredding. For DTG, the AE (10.7-15.7%) of datasets for ML model construction (**Table 5-23**) lied with AE (28.3%) of nested design (**Table 5-19**).

6.4 ML model for identification of SRF prevalent polymers

In this section, a discussion on the development of ML model for composition identification of SRF (O4) is presented in four parts: i) ML model generalization performance based on the results (Section 5.7); ii) novelty of ML model; iii) credibility of methodological approach (Section 4.3); and iv) benefits of its application in SRF sector.

6.4.1 ML model generalisation in identification of SRF composition

This research is the first version of a robust and adaptable ML algorithm able to identify SRF composition at polymer level providing a better understanding of its properties and therefore improving SRF QA/QC. Specifically, TG-DTG and FTIR techniques were used as fingerprinting tools to develop the ML model able to identify the content of seven prevalent polymers in SRF (Obj:4).

Firstly, applicability of the model in artificially prepared samples with similar composition to SRF at polymer level was verified with cross-validation under an analytical precision 91.7% (Table 5-23). Cross-validation indicated that ML model yielded to a sufficient goodness-of-fit with $R^2 > 0.76$ for all seven polymers (Figure 5-40). A rule of thumb is that an $R^2 > 0.7$ is good (Rumsey, 2007; Henseler et al., 2009), but it depends on the application area. In PVC, residuals of the training set had an intension to be arranged in parallel to the y-axis at the edges of the trend lines (Figure 5-40). This phenomenon indicated that the model yielded to poorer prediction performance at the upper and lower bounds of PVC. Considering the cross-validation error (Figure 5-39), the ML model yielded to higher prediction for cellulose (SMAPE: 13%), lignin (SMAPE: 24%), HDPE (SMAPE: 23%), and PP (SMAPE: 23%) compared to xylan (SMAPE: 28%), PET (SMAPE: 30%) and PVC (SMAPE: 49%). The different prediction error between polymers (Figure 5-39) was related to their proportions in the mixtures. Less prevalent polymers in the mixtures were more vulnerable to inaccuracies (Kailkhura et al., 2019). This is exemplified by the considerably higher error (Figure 5-39) in the less prevalent polymer PVC compared to the most prevalent cellulose (Table 4-7). Interestingly, the prediction error for identification of PP and HDPE was almost identical in all sets of model construction including

training (14%), cross-validation (23%) and hold-out validation (29-30%). This might be attributed to their similar properties (Maddah, 2016; Polymer Database, 2019b; Gabbott, 2008) and thermal degradation profiles (Sørum et al., 2001; Park et al., 2012).

Secondly, hold-out validation stage verified that ML model can be applied to the identification of prevalent polymers in waste-derived materials with inherent presence of impurities and cross-contamination under an analytical precision 92.3% (**Table 5-23**). In **Figure 5-40**, the hold-out validation set provided a substantial goodness of fit for all of the components with $R^2 > 0.62$ for all polymers. It is worth mentioning that in case of xylan, the residual that exceeded the upper bound of training set (**Table 4-12**: 4th design point:) led to a diversion of the hold-out trend line from the training line (**Figure 5-40**) indicating that the ML algorithm is weak to make predictions outside the design region (Zhang et al., 2019).

Despite the limitation to accurately determine the proportions of biopolymers in the hold-out validation set (**Section 4.3.7**) using typical reporting values (**Table 5-5**), the identical and relatively low error between cross-validation and hold-out validation (**Figure 5-39**) for biomass identification (SMAPE: 10%) indicated that ML model could generalize well in biopolymers. From the perspective of plastic fraction, the difference between cross-validation and hold-out validation was higher (SMAPE: 17% vs 24%) still negotiable. **Figure 5-38** showed that the hold-out validation error for the identification of biomass (SMAPE: 10-12% for both datasets) was notably lower compared to cellulose (SMAPE: 20-23% for both datasets), which was the most prevalent biopolymer in the entire design region. This indicated that the actual proportions of biopolymers in the validation mixtures might considerably differ from the reported proportions. For the identification of plastic fraction (**Figure 5-38-C**), in which the proportions of fossil-based polymers were analytically determined obtaining a more reliable estimation (**Section 4.3.7**), the hold-out validation error was in high agreement (SMAPE: 24-27%) with this of HDPE (SMAPE: 26-29%) which was the most prevalent polymer in plastic fraction.

In **Figure 5-39**, cross-validation error was lower compared to hold-out validation either at relatively low extent (SMAPE: 13% vs 20% for cellulose, 23 vs 29% for HDPE, 23 vs 30% for PP, and 35% vs

40% for PET), moderate extent (SMAPE: 28% vs 40% for xylan, and 24% vs 53% for lignin), or extreme extend (SMAPE: 49% vs 1.42 for PVC). The higher hold-out validation error compared to cross-validation (**Figure 5-39**) arise from an inevitable combination of variance and bias. In practical applications, the accuracy level of ML model performance comes from a variance-bias tradeoff defining its generalisation ability (Choy et al., 2018). In relation to the first, the slightly higher hold-out validation error with the use of the widest dataset (22nd) compared to the 20th dataset as input matrix (**Figure 6-1** and **Figure 5-38**) indicated that the high number of predictors compromised sort of model generalization (Wagner and Rondinelli, 2016). An increase of sample population can be a solution to overfitting issues, but data obtainment in materials science is expensive and laborious and therefore a compromise should be taken (Wagner and Rondinelli, 2016). In relation to the second, a part of the inflated error in hold-out validation set with waste mixtures compared to cross-validation with synthetic mixtures came from the different constitutional heterogeneity between training and validation mixtures and therefore thermal behaviour (synthetic vs waste mixtures) (Grammelis et al., 2009; Cuperus et al., 2005). High bias is attributed to erroneous assumptions in the algorithm leading to missing associations (underfitting), while high variance is due to overreaction of algorithm to low variations leading to random noise (overfitting) (Choy et al., 2018).

In addition to this, the concurrent use of MAE and RMSE in hold-out validation (**Figure 5-37**) provided useful information: the ratio of MAE to RMSE ranged from 0.87 for HDPE to nearly 1 for PVC indicating that residuals have quite similar magnitude (MAE = RMSE). The higher the difference between them the higher the variance in the individual errors in the sample (Willmott and Matsuura, 2005). This observation implied the credibility of generalization error, although there are specific residual variance estimation techniques for this purpose (Liitiäinen et al., 2009).

Finally, the generalisation of the model in commercially produced SRF samples including not only impurities and cross-contamination, but also a wide variety of other unidentified materials (e.g. fines, inert, other polymers, etc.) was also examined (**Section 5.7.7**). Surprisingly, SMAPE of both biomass and fossil-based fractions was lower in testing set (**Figure 5-41**) compared to cross- and hold-out validation set and almost identical with SMAPE of training set (**Figure 5-39**). This means that the

model randomly fits better to the test set (**Figure 5-42**) rather than the validation sets and equally well to the test and training set (**Figure 5-40**). This might be partially related to the small sample population of the testing set ($n=4$) and therefore difficulty to detect profound effects, still it indicated the high potential of ML model to generalize sufficiently to SRF under an analytical precision 91.3% (**Table 5-23**).

In addition to polymer identification, the possibility to extend ML model's generalisation from the identification of PVC to Total [Cl] was examined. Results showed that the model has potential to identify Total [Cl] in SRF interpreting as PVC. This was observed by the considerable reduction of forecast error when the amount of PVC (SMAPE: 142%) was converted into Total [Cl] (SMAPE: 74%) in the hold-out validation stage (**Figure 5-39**). Hold-out validation set consisted of waste mixtures which had higher Total [Cl] than the corresponding amounts of PVC added into them. In waste mixtures, PVC was not the exclusive source of Cl unlike to synthetic mixtures due to cross-contamination of waste items (e.g. wood and paper) by Cl or presence of impurities (see **Table 5-3**). In cross-validation, the forecast error was identical between PVC and Total [Cl] (SMAPE: 49%) since PVC was the exclusive source of Cl in the training set.

The inclusion of the FTIR technique, by which Cl can be qualitatively identified (e.g. aliphatic chloro-compounds: C-Cl stretches appear from $850-550\text{ cm}^{-1}$ (Bacsik et al., 2008)) allowed the model to learn from the results and improve the testing cycle (Monserrat et al., 2020). Noted that for the identification of PVC as a fossil-based polymer without considering its Cl content, TG-DTG dataset was sufficient on its own. In **Figure 5-22** and **Figure 5-27**, the slightly better performance of dataset combinations that did not include FTIR (1st and 4th) was due to the fact the TG-DTG thermogram of PVC considerably differs from the other fossil-based polymers (**Table 2-7**), resulting in the ability of ML algorithm to identify the amount of PVC without FTIR.

6.4.2 ML model for identification of SRF composition: a novel tool

ML models are adaptable, data-driven – automatically learn and improve from experience (Monserrat et al., 2020) – enabling to be practical tools and abreast of changes in evolution of underlying practice

patterns (Kalet et al., 2020). For that reason, ML models have started to attract the interest of medicine as QA tools, e.g. for dose optimization in computed tomography (Meineke et al., 2019) or online adaptative radiation therapy of prostate cancer (Zhang et al., 2016). Yet, ML algorithms for QA in SRF has gained no attention. Only two studies that could be considered a step towards that perspective were found. The first study developed a ML model using TGA-FTIR-MS results (through artificial neural network) able to predict thermal behaviour of RDF at new heating rates without performing experiments, a potentially useful tool for kinetic analysis (Çepelioğullar et al., 2016). The second study developed a ML model using process variable and elemental analysis able to predict the lower heating value and syngas yield from MSW in a fluidized bed gasifier, a functional tool in thermochemical processes (Pandey et al., 2016). In relation to this, there is one more recent study that constructed a ML model (least-square support vector) that identified the HHV of MSW using data from elemental analysis (Rostami and Baghban, 2018). These studies demonstrate that ML has started to gain attention by waste sector more and more.

To the best of my knowledge this is the first time of such a QA tool, a ML model able to identify SRF composition based on its prevalent polymers. So far, insights into the composition of commercially produced SRF samples were obtained either through manual sorting or TG-DTG (**Table 2-3**). The latter has gained attention to develop tools for composition identification of waste-derived materials. The first endeavor was by Heikkinen et al. (2004), who investigated the thermal degradation profiles of waste components with the use of TG-DTG and applied the WSM (**Eq. 2-1**) to identify the composition of waste mixtures based on three waste component categories: low stability organic, lignocellulosic and plastic materials (Heikkinen et al., 2004). The shares of these waste categories into unknown waste mixtures were calculated by correlating the TG-DTG thermograms of single categories with these of waste mixtures using an excel add-in solver (what-if analysis) (Heikkinen et al., 2004). However, WSM has been criticized for its suitability in waste mixtures due to the presence of interaction effects especially between PVC and cellulose (Sørum and Task, 2001; Grammelis et al., 2009; Ma et al., 2019; Matsuzawa et al., 2001; Yu et al., 2016; Zhou et al., 2015). A more recent research identified the composition of RDF by defining the mass loss intervals obtained from TG-

DTG thermogram based on three waste categories including cellulose volatiles (180-397°C), plastics (397-567°C) and high temperature volatiles (> 567°C) (Robinson et al., 2016).

TG-DTG is a popular tool for understanding the properties of waste-derived materials since it offers insights into both thermal behaviour, which is critical especially in co-combustion applications (Velis et al., 2010), and composition at a relatively heterogeneous waste level, this of biomass and fossil-based fraction (Grammelis et al., 2009; Skodras et al., 2009; Efika et al., 2015; Robinson et al., 2016). Still, the use of TG-DTG does not provide complete information neither on SRF thermal behaviour nor composition. The first limitation is related to the inability of TG-DTG to detect physical changes, heat flow sensitivity, gas emissions and corrosion potential during thermal decomposition (Heal, 2002; Efika et al., 2015). To obtain insights into these reaction-related properties a combined system of simultaneous thermal analysis (STA) and evolved gas analysis (EGA) techniques under a strict sampling and sample preparation protocol is required leading to a specialised laboratory analysis, which is a no cost-effective approach. In relation to the second limitation, the presence of considerable overlapping degradation areas amongst polymers depending on the operating conditions (Ray and Cooney, 2018) leads to missing information. TG-DTG profiles of complex mixtures at multiple levels including an assembly of waste items, materials and chemical compounds (**Section 2.4.1**) revealed overlapping thermal degradation areas (**Figure 5-44**). For example, under the most prevalent TGA operating conditions (**Figure 5-6**), prevalent SRF polymers overlap in a range that leads to overlapping degradation areas between biomass and fossil-based fraction and therefore a biased estimation of SRF composition at this level (**Figure 5-44**).

Manual sorting widely used for composition identification of SRF (Stępień et al., 2019; Nasrullah et al., 2016; Porshnov et al., 2018; Hilber et al., 2007b) is a tedious and time-consuming technique that identifies the composition at a waste component category level (e.g. specific *paper/cardboard* categories, *wood*, specific *plastic* categories, *textiles*, *finer*, etc.) (Séverin et al., 2010). Manual sorting introduced uncertainty due to grouping heterogeneous waste categories (Séverin et al., 2010) resulting in inability to identify complex waste items consisting of mixtures of biomass and fossil-based materials (BS EN 15440, 2011) and the considerable amount of fines, which can reach up to 40% w/w

of total SRF mass (Sarc et al., 2014). This level of uncertainty is affected by the size and PSD of the particles in the sample (Kaartinen et al., 2013). Manual sorting is most commonly applied in determination of input waste composition of the flows in MT/MBT plants (Velis et al., 2010). However, in commercially produced SRF samples with a typical particle size at 30-40 mm following end-users specifications (Velis et al., 2010), manual sorting is difficult and inefficient, whilst for SRF briquette samples it is impossible.

This ML model is the first tool that provides reliable information on SRF composition at polymer level for the total mass of the samples without considering any assumption (e.g. no interaction effects or specific degradation ranges of components). By comparing ML model performance with manual sorting and TG-DTG at level of biomass and fossil-based fraction (**Table 5-22**), it was revealed that TG-DTG identified less amount of biomass and plastics in SRF samples (64.7-74.7% w/w) than manual sorting (76-80.1% w/w). Still, with manual sorting a proportion of the sample remains unidentified, while ML model performs material identification to the entirety (i.e. 100%) of sample mass. A current weakness of the model is that it identifies the composition considering only these seven polymers, still the most prevalent able to represent the typical SRF composition. This can be improved by adding more components in the model.

The measurement of mass percentages of biomass and fossil-based fraction can provide information on SRF biogenic content and therefore the ML model could also be used for this purpose. Besides, TG-DTG was recommended for the determination of renewable energy content in RDF by Robinson et al. (2016), whilst manual sorting is a standardised technique for the determination of biogenic content in SRF (BS EN 15440, 2011). However, manual sorting has been compared with the selective dissolution method by Séverin et al. (2010) reporting the superiority of the latter. All three methods – ML model, TG-DTG, manual sorting – determine the biogenic content on a mass basis, but for CO₂ trading matters and renewable or renewable energy incentives the biogenic content should be converted into carbon or calorific content basis increasing the uncertainty and the cost (IEA, 2012).

6.4.3 Credibility of methodological approach for the development of ML model

The development of the ML model originated from a novel methodological approach that determined its creditability. The greatest part of the results (**Section 5.7**) referred to decisions taken at each stage of model construction following a series of design, experimental and computational methods using domain knowledge (**DoE2: Section 4.3**). To make sense of model decisions, a discussion from methodological perspective including comparative evidence and limitations is useful.

In DoE, ML methods are particularly helpful for processing wide datasets, that have a considerably higher number of predictors compared to sample population, even under a non-carefully controlled design, due to minimal assumptions about the data generating system (Bzdok et al., 2018). However, the absence of domain knowledge may lead to incorrect ML predictive models (Wagner and Rondinelli, 2016). In materials science, the development of reliable ML models requires the attention to five critical aspects: i) collection of data relevant to property (Wagner and Rondinelli, 2016); ii) representative sub-sampling (Kailkhura et al., 2019); iii) selection of suitable ML algorithm; iv) model training strategy (Cawley and Talbot, 2010), and v) evaluation of generalization performance (Kailkhura et al., 2019). Herein, all these aspects were thoroughly examined to ascertain the validity of the ML model.

In relation to (i), special attention was paid to the formulation of a design region able to represent typical SRF composition (**Table 4-8**). This was achieved by constructing an optimal mixture design with the use of the advanced Design-Expert software dedicated to DoE. The selection of complex constraints led to a relatively narrow and representative design region (**Table 4-7**), while the selection of a simplex lattice design would provide mixtures divergent from SRF composition. Traditional modelling methods such as binary mixtures would not allow representation of the inside of inherent heterogeneous materials precisely, while additional information assigned to each of the design points (complex constraints) led to a direct representation of parametric curves and volumes (Li et al., 2020). High-quality ground truth training data is not less important than the sample population (Choy et al., 2018). This methodology was also applied by a previous research that implemented optimal mixture design to develop a mathematical prediction model of kinetic parameters of biomass with the use of

TG-DTG (Zhang et al., 2016). The proportions of biopolymers were optimised using Design-Expert software and TG-DTG experiments were performed with biomass mixtures (Zhang et al., 2016).

At this stage of DoE, the main limitation was to regulate the number of components taking into account the waste level, so that to receive an affordable number of required mixtures. The selection of a sufficient number of micro-features considered typical of the entire material is a recommended approach on modelling of inherent heterogeneous materials, since it is hard to analyse all of them in reality (Ye and Yu, 2010). The representation of SRF composition at polymer level resulted in the formation of a training set accurately determined. The construction of a training set at a waste component category level, e.g. *paper/cardboard*, *wood*, *plastics* and *textiles*, would lead to more heterogeneous components resulting in difficulty to control thermal behaviour and therefore to obtain the desired model performance and accuracy (Li et al., 2020).

In relation to (ii), the establishment of a fitness-for-purpose sub-sampling plan to perform TG-DTG estimating the arising uncertainty was a considerable part of this research, as discussed previously (**Section 6.3.2**). This effort concerned commercially produced SRF samples, which require adherence to a fastidious sub-sampling protocol (Prichard and Barwick, 2007). Despite the testing set came from commercially produced SRF samples, training and hold-out validation sets were not subjected to any extensive mass reduction sub-sampling process. These sets were constructed by preparing test samples with low masses (ca. 5 g) under predetermined composition. Uncertainty emerged mainly from test sub-sample to test-potion sub-sampling and analysis (AE), which was estimated by calculating the precision of analytical measurements (**Table 5-23**) and compared with a previous study (Robinson et al., 2016). High levels of analytical precision ($\geq 91.3\%$) were obtained for all datasets of model development (**Table 5-23**) providing confidence in ML model accuracy.

In relation to (iii), the MRF algorithm was selected taking into account studies that compared random forest with other related techniques (Wagner and Rondinelli, 2016). Random forest was considered an effective tool for regression in spectroscopic data having great potential for modelling linear and non-linear multivariate calibration (Ghasemi and Tavakoli, 2013; Lee et al., 2013). Specifically, Ghasemi and Tavakoli (2013) reported the superiority of random forest regression, in terms of computation

time and robustness to noise and outliers, over other related regression algorithms such as partial least squares, bootstrap aggregating of regression trees, and nonlinear support vector machine using four spectroscopic datasets. This was also confirmed by Lee et al. (2013), who compared random forest with partial least squares applied in NIR datasets of gasoline and naphtha samples for determination of octane numbers, paraffin, naphthalene and aromatic concentrations.

Still, the use of univariate random forest regression for each polymer would be less effective option than MRF. Haider et al. (2015) compared the univariate random forest with MRF applied to genomics of drug sensitivity in cancer database reporting that univariate random forest generated a deterministic predictive model for each drug that ignored the relationship between different drug sensitivities during model development. MRF incorporated the relationships between different output responses providing higher model accuracy (Haider et al., 2015). This statement was confirmed here since MRF did not violate the equality constraint (**Eq. 4-7**), but provided predicted values for polymers the summation of which was equal to 100% (**Table 5-21**).

Results from hyperparameter tuning underpinned that the process is far from established (**Section 0**). The lack of information on MRF made hard to obtain conclusive remarks on which approach (**Section 4.3.6.2**) was better for handling several dataset combinations. This is in agreement with a review research on random forest and software implementation for water scientists reporting that the optimal value of *mtry* is controversial (Tyrallis et al., 2019). The second approach used a variable *mtry* proportional to the number of predictors. However, the relationship of the number of predictors with *mtry* did not seem to be proportional ($mtry = 1/3p$) as implied by researchers (Zhang et al., 2019; Tyrallis et al., 2019; González et al., 2016; Liaw and Wiener, 2002). In hyperparameter tuning, optimal *mtry* was 30 for the 22nd dataset with the highest number of predictors (**Figure 5-32**), while *mtry* was 40 for the 20th dataset (**Figure 5-35**). This indicated the correlation of TG and DTG data included in the 22nd dataset as optimal *mtry* value can be lower for correlated predictors (Gareth et al., 2013). This correlation amongst TG and DTG points was also confirmed by PCA results that showed the correlation of combustion characteristic points obtained by TG-DTG thermogram (**Section 5.6.2**). Interestingly, the value of optimal *mtry* found in the 22nd dataset (30) provided the worst performance

for the 20th dataset (**Figure 5-35**). That behaviour was unpredictable and the absence of literature evidence did not let to provide any explanation.

Despite some fluctuations between *Ntree* and prediction error examined in both datasets (**Figure 5-31** and **Figure 5-34**), the increase of *Ntree* did not induce any significant improvement in the model above the default value (500). This observation is in agreement with a previous study in spectra data acquired from fossil-based products, in which *Ntree* values below to 200 provided higher prediction error (Lee et al., 2013). Additionally, *Min_Leaf* seemed to notably affect model performance (**Figure 5-33** and **Figure 5-36**), while it was considered as a less important parameter compared to *Ntree* and *mtry* (Tyralis et al., 2019; Segal and Xiao, 2011). These finding clearly indicated that future attention need to be paid to the stage of hyperparameter tuning of MRF regression for the acquisition of stronger models.

Results from data pretreatment techniques for MRF (normalization and FTIR smoothing) indicated that they might be useful, but not for each case. For example, data normalization was beneficial for lignin and PP identification (**Figure 5-22** and **Figure 5-27**). This was confirmed from Dinç et al. (2014) who reported that normalisation might improve the performance of random forest models. The reason that normalization worked for these two specific components might have a relation with the fact that their degradation profiles are highly masked by others due to either high similarities (e.g. this of HDPE with PP (Sørum et al., 2001; Park et al., 2012)) or low signal (e.g. lignin (Zhang et al., 2016)). However, normalised datasets had poorer performance (**Figure 5-24**) than raw datasets (**Figure 5-23**) for polymers with low proportions in SRF including xylan, PET, and PVC, while for the most prevalent polymers (HDPE and cellulose) the prediction error between normalized and raw datasets was quite similar. In addition, FTIR smoothing techniques did not provide any significant improvement to model performance (**Figure 5-24**), but it is possible other techniques reported by Gautam et al. (2015), not applied here, to perform better.

In relation to (iv), the performance of model training was methodically examined through a series of dataset combinations and validation procedures so that to generate a list of candidate datasets for training set considering overfitting issues. Repeated training of ML models using different sets of

hyperparameter values and available data are important for a trustworthy performance evaluation of model training (Cawley and Talbot, 2010). Herein, two different approaches related to hyperparameter values (**Figure 4-11**) assessed the performance for each polymer across all available dataset combinations (**Figure 5-22** and **Figure 5-27**) and each dataset across all polymers (**Figure 5-23 – Figure 5-26** and **Figure 5-28**). The stage of training showed that combinations of DTG-FTIR or TGA-FTIR datasets provided better prediction results than other combinations, while single FTIR had the worst performance (**Figure 5-22** and **Figure 5-27**). This weakness may be related to the fact that FTIR is used for qualitative identification rather than quantitative analysis, especially in mixtures with more than two components (Ji et al., 2009). Also, **Table 5-20** indicated that DTG technique was more preferable for xylan and PET than TGA which was better for more prevalent components due to the nature of DTG to capture more information and therefore changes related to decomposition of less prevalent materials (Heal, 2002).

Beyond the importance of a careful training approach, the presence of overfitting can be examined only with validation (Wagner and Rondinelli, 2016). Herein, cross-validation was implemented, which is the most attractive choice to control overfitting (Tran, 2016; Cawley and Talbot, 2010). At the first stage of cross-validation with constant *mtry* for the candidate datasets (**Figure 5-29** and **Figure 5-30**), no clear insights into the superiority of 22nd set with 12,243 predictors versus the 20th set with 7,922 predictors was provided, which was revealed after hyperparameter tuning (**Figure 6-2**). The implementation of cross-validation before hyperparameter tuning led to inability to capture slight differences of overfitting between 20th and 22nd datasets. Optimal tuning factors can considerably improve model overfitting, but their values might be different for each dataset (González et al., 2016). Noted that cross-validation should be conducted under optimal tuning values to reliably assess the model performance (Janitza and Hornung, 2018; Segal and Xiao, 2011; Zhang et al., 2019). However, at the stage of cross-validation with constant *mtry*, there were three datasets to be assessed (18th, 20th, and 22nd) with 20th and 18th having identical number of predictors (7,922), while all of them consisted of interrelated analytical data. In such situation, the cross-validation can provide insights into the superiority of 20th versus the 18th dataset (**Figure 5-29** and **Figure 5-30**) which was the purpose of

this stage without concerns, but not for the 20th versus the 22nd dataset due to different number of predictors. In the latter case, the decision was taken after hyperparameter tuning through 10-fold cross-validation (**Section 5.7.4**).

Assessment of generalization performance (v) is necessary for developing assured ML models as it provides insights into trustworthiness of regressor's prediction (Kailkhura et al., 2019), although the true trust error is generally unknown (Cawley and Talbot, 2010). For that reason, three different sets of samples were used assessing the generalisation performance of ML model: i) synthetic mixtures at polymer level similar to SRF composition (cross-validation); ii) waste mixtures under the inherent presence of impurities and cross-contamination of waste items (hold-out validation); and iii) commercially produced SRF samples (**Figure 5-39**). This methodological approach of a step-by-step validation led to define and improve the bounds of model's applicability to SRF processing sector.

6.4.4 ML model: benefits in SRF pre- and co-processing sector

The ability of ML model to identify the composition of SRF (**Figure 5-40** and **Figure 5-42**) is related to the unique and certain properties of polymers associated with their molecular composition and industrial processing production (National Research Council, 1994), which helped to obtain a better understanding of SRF properties and therefore evaluation of its quality. For example, a high proportion of cellulose indicates high proportion of office paper and natural textiles consisting mainly from cotton fibers, while similar levels of xylan and lignin comparable with cellulose intimates high proportion of wood and/or newspaper (**Table 5-5**).

ML model prediction in commercially produced SRF samples used for model testing (**Table 5-21**) showed that the fraction of biomass materials was lower for the samples collected from the first MT plant (SRF1 & SRF2: 52.0-54.3% w/w) compared to the samples from the second MT plant (SRF3 & SRF4: 55.3-59.7% w/w). In addition, samples from the first plant had higher proportions of HDPE and PP (36.0-37.9% w/w) than the samples of the second plant (31.9-35.9% w/w) indicating the presence of plastic packaging materials (**Table 5-21**). Similarly, PET proportions representing the presence of textiles were in a range of 7.8-8.2% w/w for the first MT plant and 6.4-6.9% w/w for the

second (**Table 5-21**), while PVC was 1.9-2.0% w/w and 1.8-1.9% w/w, respectively. This finding implied the presence of lower quality of plastic fraction for the first MT plant due to lower thermal stability and higher residue of PET compared to polyolefins (**Table 2-7**) and potentially elevated levels of Total [Cl] (**Table 5-3**).

The ML model is available for use by both producers (post-production) and end-users (pre-recovery) providing an ease reporting SRF quality leading to wider confidence in SRF quality and therefore efficient trading of SRF. The use of this tool is straightforward, timesaving and affordable indicating its practicality and potential of effective dissemination in SRF stakeholders. The ML model can be applied in commercially produced SRF samples using the established ML algorithm (**Appendix F**), the selected training set (**SI.4**) and analytical measurements of the testing samples (DTG and FTIR results).

The use of this tool can guide producers to deliver a quality-assured SRF able to meet the legislative requirements and market needs resulting in a sustainable material flow management. The application of ML model in MT/MBT plants can help producers to adjust input waste streams, operations and equipment, and assess these modifications with existing quality management schemes so that to produce a fuel quality that complies with specification and end-users requirements. Proper adjustment of separation unit processes can lead to an efficient redistribution of desirable properties/materials enabling their enrichment in output stream (Velis et al., 2010). The identification of quality in produced SRF samples can help producers to set an optimal tradeoff between achieving high quality of recoverable outputs and quantity of reject materials under controlled operational processing cost depending on end-users specifications (Velis et al., 2010). For example, inflated levels of PVC and PET predicted by the ML model may indicate the need of paper/cardboard introduction in the output stream increasing the technological performance of the fuel, while low levels of polyolefins may need the introduction of plastic packaging increasing its financial performance.

This new QA tool is even more important if it is taken into account the fact that the SRF producing plants have extremely limited control over their inputs, typically receiving inflows from multiple sources, varying over time and without real means to know their composition (Velis et al., 2010;

SUEZ, 2018). Systematic application over SRF sampling linked with batch control can potentially reveal the composition for different material waste providers for the MBT/ MT plants, and enable better timing and mixing for consistent SRF production, which is the most appreciated property from end-user perspective (Velis et al., 2010).

In addition, the ML model can be applied by end-users (e.g. cement kilns) before co-combustion providing wider confidence on SRF uptake. The model can help end-users to prevent risks associated with the unpredictable behaviour of the fuel during co-processing through the selection of appropriate feeding ports (e.g. low SRF quality through secondary burners) (Sarc et al., 2014) and maximum substitution rates depending on SRF quality (Beckmann et al., 2012) resulting in a waste resource- and cost-efficient decisions. SRF is typically used as mixture with fossil fuels (e.g. coal) or other homogeneous waste streams (e.g. tyres). The novel ML model tool can allow designing of mixtures of SRF with other fuels prior to combustion, to achieve optimal combustion properties customised to each cement plant needs.

7 CONCLUSIONS & FUTURE WORK

7.1. Conclusions

The work presented here resulted in the development of a novel toolkit by way of a systematic review and DoE that can be used for post-production QA in SRF; including a ML model for composition identification at polymer level, and a fitness-for-purpose sub-sampling plan ensuring the magnitude of variation in critical SRF properties. A series of conclusions presented here, in the order they appear in the Thesis, following the research objectives **(O1-4)**: i) critical review of CI in SRF co-combusted in cement kilns **(O1)**; ii) establishment of sub-sampling plan (DoE1) **(O2)**; iii) quantification of sub-sampling uncertainty (DoE1) **(O3)**; and iv) ML model for composition identification of SRF (DoE2) **(O4)**.

With a focus on the delivery and utilisation of a quality-assured SRF for a sustainable waste recovery, this research focused on advancing some of the most critical aspects to meet this requirement, as identified by the systematic review. The main outcome of this research is the creation of a novel tool (ML model) , potentially useful to both SRF producers (post-production) and end-users (pre-recovery), able to predict the composition of SRF at polymer level by analysing commercially produced SRF samples through thermal (TG-DTG) and spectroscopic (FTIR) analytical techniques **(O4)**. By quantifying the uncertainty arising from sub-sampling SRF during characterisation, including the most critical properties for market demands **(O3)** and establishing an affordable sub-sampling plan with tolerable levels of uncertainty for the different properties **(O2)**, a practical integrated characterisation scheme is therefore available to be adopted. This scheme ensures a reliable TG-DTG-FTIR characterisation of SRF and thus enables the validity of any analytical determination based tool, such as the new ML model prediction presented here. Following this integrated characterisation scheme and applying the ML model, for the first time such a compact set of information on SRF quality can be obtained with relatively high confidence and low effort.

Herein, special attention was also paid to CI in SRF, because it is a key QA property for SRF uptake; exploring its variability from multiple perspectives, including key aspects of SRF pre-processing, sub-sampling, analytical determination, and SRF co-processing. The systematic review on the variability of CI in commercially produced SRF samples **(O1: pre-processing)** helps us to understand the main

sources of Cl, which along with the knowledge gained from the characterisation scheme (**O2&O3**) enables potential customisation to a tolerable level of Cl variability (**Section 6.3.2**). By further advancing the knowledge on the fate of Cl during SRF co-combustion (**O1**: co-processing), this level can be better defined, and the adaptable new ML model can be extended, depending on future needs (**O4**). Specifically, the following conclusions were obtained, listed here by each objective (**O1-4**):

O1: The findings of this objective offer insights into the actual and perceived challenges around Cl arising from both stages of SRF pre- and co-processing, as the key limiting factor for efficient SRF trading in cement kilns. In pre-processing sector (**Section-5.1.1**), the sources of Cl in SRF (**Table 2-9**) helped to understand the variability of Cl in commercially produced SRF samples and SRF feedstock (**Section-6.1.1**). Critical review analysis suggests that despite major knowledge gaps, there is sufficient but currently underused information that could potentially allow advanced ‘design’ of SRF as a manufactured processing output with controlled and customised properties. By adopting better QA practices, SRF producers could achieve desirable outcomes, such as lowering the average Cl concentration and controlling (limiting) its variability around the mean, therefore enabling higher substitution rates and widespread application. In the co-processing sector (**Section 5.1.2**), this work advances knowledge on the fate of Cl during SRF co-combustion in cement kilns including the chemical reactions and mass distribution of Cl through the system. This improved understanding allows for the rationalisation of operating criteria for Cl mitigation by end-users (**Section-6.1.1**). Core evidence behind these conclusions was obtained and is detailed in the relevant sections:

- Evidence collated here (**Section 5.1.1**) demonstrated similar levels of Total [Cl] in SRF (0.62-0.90% w/w_d, $\alpha=0.05$) and MSW (0.65-1.36% w/w_d, $\alpha=0.05$), but variability (measured as coefficient of variation) around the average was ca. 30% lower for SRF (36.7%) in comparison with MSW (52.8%). This finding exemplifies the effectiveness of mechanical processing equipment employed in MT/MBT plants in homogenising the SRF output.
- Statistics confirmed results from other studies that have identified the generic waste categories *rubber-leather*, *plastics* and *textiles* as considerable potential sources of Cl load (**Table 5-3**). Conversely, *paper/cardboard* and *wood* were confirmed as being low in Cl

content (**Table 5-3**), and can thus be used as high fractions to lower the SRF Total [Cl] content.

- A generalised mass flow is developed here which depicts the typical Cl fate in its most prevalent forms during SRF co-combustion in modern cement kilns (**Figure 5-2**); showing that most Cl (60-73% of Cl input) remains in the system ('stock') in the form of alkali chlorides indicating a high risk of operating problems that might be induced under elevated levels of Cl. A considerable proportion is captured by baghouse filters and therefore concentrated in air pollution control dust confirming that the installation of a bypass system can considerably mitigate Cl-related operating problems. A small percentage is incorporated in the clinker as $\text{CaCl}_{2(s/l)}$ making the clinker sticky and therefore degrades its quality and generates material build-ups. Finally, SRF co-combustion does not play a critical role in the emission of gaseous pollutants due to the alkaline environment and thermal conditions prevailing in cement kilns (**Section 5.1.2**).

O2: A 'suggested' sub-sampling processing was established by using and adhering to optimal, yet practicable and affordable sampling practices and equipment. The ability of such laboratory set up and operational regime to render satisfactory measurements was verified. Therefore the established sub-sampling plan can be used as a fitness-for-purpose approach to minimise potential bias, and could be incorporated in the relevant CEN/TC 343 standards on SRF sample preparation (BS EN 15413, 2011; BS EN 15443, 2011). Core evidence behind these conclusions was obtained and is detailed in the relevant sections:

- Experimental results (**Section 5.4.3**) showed that the established sub-sampling plan led to representative analytical results related to the determination of MC (relative range < 4.6%), an analyte with relatively low variability. However, in the case of Total [Cl], obtaining one test sub-sample entails the risk of incorrect classification of SRF (**Figure 5-12**). Less than 20% of total population of test sub-samples were not representative, assessed as exceeding the 15% upper limit suggested by the literature (**Table 5-10**). However, the selection of this limit value was arbitrary as there is no relevant comparative evidence in the solid waste management

sector (**Section 6.2**). The probability of obtaining a non-representative test sub-sample under the current sub-sampling plan and reference limit value ($> 15\%$) was between 7 and 43% (95% confidence) (**Table 5-11**), whereas drawing and averaging two test sub-samples, considerably reduced that likelihood between 2 and 9% (95% confidence) (**Table 5-13**). However, the cost and time taken to carry out sub-sampling and analysis would increase.

- The effect of shredding on representativeness of test sub-samples was determined by comparing three different sample preparation scenarios through ToS nomographs Total [Cl] (**Section 5.4.1.2**). Primary shredding ($d_{90} \leq 0.4$ cm) resulted in 11 times less sub-sampling uncertainty, expressed as FE, compared to a non-shredded test sub-sample. The cryogenic, final shredding stage ($d_{90} \leq 0.15$ mm) applied to the test sub-sample reduced the uncertainty more than 3 times compared to primary shredding scenario (**Figure 5-9**). Therefore cryogenic shredding is a both effective and highly recommended sample preparation process step for chemical analysis of waste-derived materials that featuring high inherent heterogeneity such as SRF (**Section 6.2**). The configuration settings of the cryomill had a negligible effect on the decrease of the overall uncertainty (**Section 5.4.1.1**) indicating that the most economical settings can be used, for example with low number of grinding cycles, reducing processing time and liquid nitrogen consumables cost.
- Practices related to shredding that could introduce bias were negligible as long as the suggested sub-sampling plan was carefully executed: (1) shredding did not affect the MC, assuring the validity of analyte determination on a dry reporting basis (**Section 5.4.2.1**); (2) the loss of sample mass was negligible (0.7% w/w) – but, the operator’s experience and diligence is crucial, is crucial and mass loss could be higher if attention is not paid to best practice (**Section 5.4.2.2**); and (3) the recovery of Total [Cl] from cryogenically shredded test portions of artificial SRF comprising a mixture of reference materials reached 98.3% – an acceptable level of analytical error (**Section 5.4.2.3**).

O3: The overall uncertainty (RSD) arising from laboratory sampling, sample preparation and analytical determination under the established sub-sampling plan for critical SRF properties including

MC, Ash, NCV, Total [Cl] and combustion behaviour (TG-DTG) through DoE1 was quantified. The work presented here can set the basis for the introduction of statistically informed sub-sampling standards in SRF characterisation, and enable the informed revision of existing technical standards that apply ToS, such as the BS EN 15442. This work can also be used for assessing the performance of sub-sampling protocols for waste-derived materials and the compliance with QA specifications, which require (or should require) the inclusion of uncertainty level along with SRF characterisation. Core evidence behind these conclusions was obtained and is detailed in the relevant sections:

- Via quantification of sub-sampling uncertainty, it was established that overall, it is feasible to obtain sufficiently representative analytical results for certain key fuel properties in SRF (moisture, ash and calorific value: $RSD \leq 6.1\%$) (**Figure 5-13**), which are more uniformly dispersed compared to other analytes such as PTEs and Total [Cl], as CEN standards stipulate. However, for the determination of Total [Cl], which is a less uniformly dispersed property and the key limiting factor of SRF end-uses, the sub-sampling uncertainty was far from negligible ($RSD: 18.2\%$). Whereas this level of uncertainty was three times higher than the other key properties, it was just above the indicative limit of 15%, suggested as acceptable in the literature. The outcome for Cl indicated that we could possibly have to live with that level of uncertainty when determination of Cl in SRF and similar properties in commercially produced SRF samples is conducted. This conclusion considered as fitness for purpose criteria (**Section 6.3.2**) the fact that: (i) SRF is inherently a highly heterogeneous material; (ii) Cl varies widely between SRF components (e.g. different types of plastic); and (iii) what is practicable for compliance statistics as established in the relevant SRF classification standard. Indeed, an RSD at 18.2% indicated that the measured Total [Cl] in a test sub-sample can range from 0.89 to 1.29% w/w_d, which corresponded to a concentration difference of 0.20% w/w_d from the average value (1.09% w/w_d) (**Table 5-14**). Putting this into perspective, the intervals between the class codes of the classification scheme of SRF for Cl are defined with ranges of 0.4-1.5% w/w_d (**Section 6.3.2**).

- Considerable level of uncertainty was estimated for determination of TG-DTG thermogram of SRF (RSD_{pooled} : 32.2%), whilst for TG thermogram the uncertainty was 11.6% and for DTG was 44% (**Table 5-19**). Still, by capturing the most critical points from TG-DTG curve able to characterise the combustion profile of the sample, the uncertainty did not exceed the reference acceptable limit (RSD_{pooled} : 7%) for most of them (35 out of 38 points) (**Table 5-18**). The highest uncertainty (RSD: 21.5%) was observed at the maximum rate of thermal degradation of the plastic fraction (3rd DTG peak) indicating the variable composition of fossil-based materials in SRF (**Figure 5-20**). TG-DTG critical points captured ca. the one half of uncertainty of entire TG thermogram, while DTG points captured only one sixth of uncertainty of DTG thermogram (**Section 6.3.3**). Considering the relatively tolerable levels of sub-sampling uncertainty for determination of critical combustion characteristics, the inherent heterogeneous composition of SRF, and the very low amount of test portion required for TGA (mg scale), the established sub-sampling plan can be considered that fits the purpose of thermal analysis of SRF.
- The relative contribution of sources including the stages of riffle splitting and analysis to uncertainty were also identified for all critical SRF properties. Nested design confirmed the reported evidence that sub-sampling uncertainty can significantly exceed the uncertainty associated with the analytical method in highly heterogeneous materials (**Section 5.5.3**). For the determination of classification properties (MC, ash, Cl, and NCV), the uncertainty introduced at the final stage (AE: from the test sub-sample to test portion) constituted only 7-13% of total sub-sampling uncertainty (**Figure 5-16**). This was just around 1/10th of the overall uncertainty: most of the uncertainty was introduced in the preceding sub-sampling stages. This finding confirms ToS proponents with regards to the need to establish an appropriate sub-sampling plan that is able to limit and control the emerging uncertainty, as far as possible (**Section 6.3.1**). For TG-DTG (**Section 5.6.3**), the contribution of AE was more evident (35.9%) stressing the importance of cryogenic shredding applied in test sub-samples (**Section 6.3.3**).

- Tangible insights on the applicability of the ToS in the context of waste samples were obtained (**Section 6.3.1**). The nested design (statistical approach) confirmed the ToS (theoretical approach) with respect to: i) the increase of uncertainty as the sample mass decreased (higher RSD at final stages); and ii) the dependence of sub-sampling uncertainty on the concentration of analytes (highest RSD found in Total [Cl] with the lowest fraction in SRF – lowest uncertainty found in MC with the highest fraction). However, the ToS-based formula needs to be re-evaluated and possibly adjusted for applications in sub-sampling of waste-derived materials, since: i) the relative contribution of sub-sampling stages to the overall uncertainty was found to differ depending on fuel property, contrary to what the ToS stipulates; and ii) the ToS-based formula overestimates the uncertainty emerging from stages without shredding (1st and 7th stage) leading to excessive effort and cost. This overestimate could be attributed to the ToS uncertainty formula being proportional to the cube of particle size ($FE \propto d^3$), which may not be universally applicable to all waste item fragments. Shredding decreases the thickness of flat or hollow particles mainly included in SRF to a lower degree compared to granular materials, for which the ToS formula was developed.

O4: The development of a robust and adaptable ML model for composition identification of SRF at polymer level provided a novel and practical tool for QA of SRF able to deliver a fuel that complies with quality requirements and market demands, enabling producers to control their input waste streams and unit operation settings and end-users their substitution rates. The ML model is able to identify seven prevalent SRF polymers including biopolymers (cellulose, xylan, and lignin) and fossil-based polymers (HDPE, PP, PET, and PVC) providing a sufficient generalisation estimated from synthetic matrices to commercially produced SRF samples (**Section 6.4.4**). Core evidence behind these conclusions was obtained and is detailed in the relevant sections:

- Cross-validation indicated the sufficient applicability of ML in mixtures consisted of artificially prepared polymers resembling SRF composition (**Section 6.4.1**). R-squared values as a goodness-of-fit measure were relatively high (> 0.76) (**Figure 5-40**), whilst evaluation metrics provided a lower prediction error for cellulose (SMAPE: 13%) followed by HDPE

and PP (SMAPE: 23%), lignin (SMAPE: 24%), xylan (SMAPE: 28%), PET (SMAPE: 30%) and PVC (SMAPE: 49%) (**Figure 5-39**). The poorer ML performance mainly on identification of PVC was attributed to its low proportion in the mixtures (0.3-3% w/w).

- Hold-out validation verified the applicability of ML model to waste-derived materials that have a more complicated composition compared to synthetic mixtures (**Section 6.4.1**). A substantial goodness-of-fit was observed for all polymers ($R^2 > 0.62$) (**Figure 5-40**). The prediction error was almost identical to the cross-validation for biomass fraction (SMAPE: 10%), indicating that model generalises well in the identification of biopolymers, and fairly well for HDPE (SMAPE: 29%), PP (SMAPE: 30%), and PET (SMAPE: 40%) (**Figure 5-39**). The model performance for the identification of PVC was substantially poorer for waste mixtures than for synthetics (SMAPE: 0.49 vs 1.42). However, by converting the quantity of PVC into Total [Cl], a substantial drop of error was found (ca. 50%) because PVC is not the exclusive source of Cl in waste mixtures due to impurities and cross-contamination. This finding indicated the adaptability of ML model to learn from experience and therefore improve its accuracy by introducing more information.
- The generalisation of the ML model when applied to genuine SRF samples was assessed for the biomass and fossil-based fraction indicating the high potential of ML model to generalise well in commercially produced SRF samples (**Section 6.4.1**). Goodness-of-fit results ($R^2 \approx 0.90$) (**Figure 5-41**) and prediction errors for biomass (SMAPE: 6%) and fossil-based fractions (SMAPE: 11%) (**Figure 5-42**) obtained by model testing with SRF samples were almost identical compared with those obtained in the training stage. Despite the small sample population ($n=4$) and the inability to accurately determinate the composition of SRF with manual sorting that did not let to detect sensitive effects (**Section 4.3.7**), similar prediction results between training and testing verified the efficient applicability of the ML model in SRF sector (**Section 6.4.1**).
- Despite the very limited research related to the selected ML algorithm (MRF regression), optimal mixture designs, and guidelines for developing a reliable ML model, a credible

methodological approach was followed including: i) a well-defined design region; ii) a fitness-for-purpose sub-sampling plan with controllable analytical precision; iii) repeated model training under a series of tuning parameters and available dataset combinations subjected to data pre-processing techniques (normalisation and smoothing); and iv) step-by-step validation with at least one independent dataset (e.g. hold-out) (**Section 6.4.3**). This methodological approach is strongly suggested for development of ML models applied in real data for material identification purposes.

- Insights were also obtained into the impact of tuning parameters on performance of MRF regression (**Section 6.4.3**) indicating that: i) optimal *mtry* was strongly dependent on the nature of training dataset with the correlation amongst predictors being more significant than the number of predictors; ii) *Ntree* did not induce any further model improvement after a certain value, with the default value (500) being appropriate in most cases; and iii) optimal *Min_Leaf* had considerable impact on prediction improvement revealing its underestimation by literature that considered *Min_Leaf* less important than the other two tuning parameters.

7.2. Future work

Future research is recommended from three main perspectives: i) research gaps identified in literature review but have not been investigated in the present study; ii) investigation of points that would be beneficial to enhanced methodological understanding; and iii) research questions arising from the conclusions.

In relation to the first perspective, future work can be conducted in the following research areas:

- A field investigation of the impact of feeding ports and substitution rates on the fate of Cl during SRF co-combustion in modern cement kilns, the main SRF end-users, is necessary to create a wider confidence in SRF uptake.

- The above knowledge could be combined with research investigation on developing technologies and strategies that could handle other sources of Cl apart from PVC to further reduce the variability of Cl in SRF.
- There is the need to standardise TG-DTG technique for the determination of thermal stability of SRF assuring its quality.

In relation to the second perspective, future work could be combined with the novel methodological principles applied here providing an in-depth understanding of such QA toolkit:

- There is the need to gain concrete understanding on what could constitute an acceptable level of sampling and sub-sampling uncertainty for characterisation of waste-derived materials depending on fitness-for-purpose requirements. This work would provide a clear understanding on what could be considered as a representative sample.
- Assessment of the performance of ML model by implementing the dimensionality reduction technique (variable importance) and the integrated MRF, a new version of MRF that provides an integrated prediction from different data subtypes, is strongly recommended. This work could be compared with the present model performance resulting in potential improvement of model accuracy.
- Research attention to MRF regression and hyperparameter tuning would optimise the process of such model construction in terms of time consumption (computation time) and effort (data pre-processing).

In relation the third perspective, the conclusions of the present work broaden the research horizon for further improvement of QA in SRF sector:

- Incorporation of the established sub-sampling plan in related CEN/TC 343 standards through a Round Robin verification test.

- Extension of the methodological approach for quantification of uncertainty (DoE1: nested design) in SRF properties with higher or unknown variability compared to the selected properties, which are critical for its quality, e.g. PTEs and elemental content (C, H, N, O).
- In combination with the before-mentioned recommendation, introduction of statistically informed sub-sampling standards in SRF characterisation (e.g. obtainment of two test-samples or more replicates) following the methodological principle of DoE1 as guiding principles can be conducted.
- Revaluation of ToS-based formula before applications in sampling of waste-derived materials and potential adjustments may lead to informed revision of existing sampling standards based on ToS.
- Exploitation of the ability of ML model to be adaptable in new data by introducing more information. This can be achieved by increasing the sample population of the existing training set with mixtures that contain additional characteristic materials that can be found in SRF intensifying the presence of Cl (e.g. addition of NaCl), impurities (e.g. addition of inert materials), and unidentified compounds (e.g. addition of PS or Nylon-6).

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APPENDICES

APPENDIX A: Recommended values for factors of sampling constant by ToS

Table A-1. Liberation parameter, l , estimates by material description. Adopted by Gerlach and Nocerino (2003)

l	Type of material
1	Analyte 100% available (recommended for most environmental applications when no criteria are available)
0.8	Very Heterogeneous
0.4	Heterogeneous Material
0.2	Average Material
0.1	Homogeneous Material
0.05	Very Homogeneous Material

Table A-2. Shape factor, f , estimates by material description. Adopted by Gerlach and Nocerino (2003)

f	Type of material
≥ 1	Needle-like materials, such as asbestos
1	All of the particles are cubes (by definition)
0.5	All of the particles are spheres; most minerals; most hazardous waste samples
0.2	Soft homogeneous solids, such as tar, or gold flakes.
0.1	Flaky materials, like mica

APPENDIX B: Background on key requirements to use ANOVA

The use of ANOVA involves certain key assumptions (Montgomery, 2017):

- I. Normal distribution of data: Analysis of variance is a parametric test assuming that data fits the normal distribution, although ANOVA is not affected too much by this violation (Harwell et al., 1992);
- II. Independence of errors: The validity of ANOVA test depends on the independence of errors (i.e. error or residuals). This requirement can be satisfied by implementing randomization in the stage of experimental design, which eliminates the source of bias (Montgomery, 2017);
- III. Normal distribution of errors: ANOVA test is affected by the normal distribution of error, especially in case of random effect model, such as here.
- IV. Homogeneity of variances (HOV): ANOVA test assumes that the variances among groups are equal. Two common tests were used for checking the HOV requirement, the Levene's and Cochran's C test. However, it has been reported that these tests may not be very robust, as they rely on HOV assumption making not clear their robustness in the presence of heterogeneity of variances (Glass and Hopkins, 1996). However, the assumption of HOV is not so crucial for balanced designs (equal n) (Bathke, 2004).

APPENDIX C: Establishment of fitness-for-purpose sub-sampling plan

C1. Statistical background on the binomial proportion confidence interval

Binomial proportion is defined as the ratio of number of successes to the sample size. The most common method for the calculation of confidence interval for binomial proportion is the normal approximation method, often referred as standard Wald confidence interval, which is given by the following equation (Brown et al., 2001; Dunnigan, 2008):

$$\hat{p} \pm z_{\alpha/2} \sqrt{\frac{\hat{p}(1 - \hat{p})}{n}} \quad \text{Eq. C1-1}$$

where $\hat{p}$ is the proportion of successes, α is the significance level, $z_{\alpha/2}$ is the z value for desired level of confidence (e.g. 1.96 for 95% confidence) and n is the sample size.

Herein, 13 out of 16 SRF sub-samples were representative (**Table C4-1**), which was equal to a proportion of 0.8125. Thus, $\hat{p} = 0.8125$. A rule of thumb for using the above formula is to ascertain that $n\hat{p} \geq 5$ and $n(1 - \hat{p}) \geq 5$, which is based on the central limit theorem (Ramachandran and Tsokos, 2009). However, this condition was not satisfied here as $n(1 - \hat{p}) = 3$. In that case, an alternative method can be used known as exact Clopper-Pearson method (Krishnamoorthy and Peng, 2007). The following equation is used for the calculation of confidence interval (Dunnigan, 2008):

$$\left[1 + \frac{n - x + 1}{x} F_{2(n-x+1), 2x, a/2} \right]^{-1} \leq p \leq \left[\frac{1 + \frac{x+1}{n-x} F_{2(x+1), 2(n-x), a/2}}{\frac{x+1}{n-x} F_{2(x+1), 2(n-x), a/2}} \right]^{-1} \quad \text{Eq. C1-2}$$

where x is the number of successes, n is the sample size and $F_{(d1, d2, a/2)}$ is the $a/2$ quantile from the F-distribution with d1 and d2 degrees of freedom.

Clopper-Pearson method is quite conservative and tends to provide wide intervals. A compromise between the two methods for the calculation of confidence interval for binomial proportions is the Wilson score method that can be used for small sample sizes ($n < 30$) (Dunnigan, 2008; Brown et al., 2001). Wallis (2013) explicitly discussed and evaluated these three methods reporting that Wilson

score method robustly depicts the uncertainty across all values of observed probability even when n equals to one. Specifically the confidence interval is calculated as follows (Brown et al., 2001):

$$\frac{\hat{p} + \frac{z^2}{2n}}{1 + \frac{z^2}{n}} \pm \frac{z}{1 + \frac{z^2}{n}} \sqrt{\frac{\hat{p}(1 - \hat{p})}{n} + \frac{z^2}{4n^2}} \quad \text{Eq. C1-3}$$

C2. ANOVA results and diagnostic checking for the configuration settings of secondary shredding

For the statistical comparison amongst the configuration settings of cryogenic shredding, key requirements for the conduction of ANOVA test were mostly fulfilled. However, certain PSD metrics (d_{50} and d_{90}) do not fit the normal distribution – assumption I – (**Table C2-1**), although the ANOVA is not very sensitive to this violation (Harwell et al., 1992). The most important is assumption III which is fulfilled here (**Table C2-1**). In addition, the p value is less than 0.05 in case of homogeneity of variance (HOV) – assumption IV – for most of the PSD metrics (**Table C2-2**). However, the assumption of HOV is not so crucial for balanced designs (equal n), such as here (Glass et al., 1972). **Table C2-3** shows ANOVA results indicating that there is statistical difference amongst cryogenic shredding programs regarding all PSD metrics.

Table C2-2. Anderson Darling test for examination of normal distribution of data and residuals (significance level $p < 0.05$) for the detection of statistical difference amongst 4 different shredding programs of secondary shredding applied in SRF: Assumptions II and III

PSD metric	p-value of raw data*	p-value of residuals**
d_{10}	0.06	0.43
d_{50}	0.03	0.41
d_{90}	0.03	0.99
Span	0.13	0.84

*Anderson Darling p values of raw data - experimental results (if $p > 0.05$ then normal distribution is assumed); **Anderson Darling p values of residuals after nested ANOVA (if $p > 0.05$ then normal distribution is assumed)

Post hoc test detects: the statistical difference for each pairwise comparison of nested sub-samples that led to the rejection of null hypothesis; and any pairwise difference that was not captured by the test of significance of ANOVA (Keppel and Wickens, 2004; Montgomery, 2017). Post hoc test was

carried out through the Tukey test (**Table C2-4**) showing that all shredding programs statistically differ from each other.

Table C2-3. Examination of homogeneity of variance (HOV) based on Levene's test (significance level $p < 0.05$) for the detection of statistical difference amongst 4 different shredding programs of secondary shredding applied in SRF: Assumption IV

PSD metric	p-value of Levene's test
d ₁₀	0.03
d ₅₀	0.04
d ₉₀	0.02
Span	0.30

Table C2-4. Tests of Significance of one-way ANOVA for four different shredding programs employed by secondary shredding at a significance level $\alpha = 0.05$

PSD metric	SS	MS	F	p-value
d ₁₀	24.3	8.1	5301.5	0.000
d ₅₀	10683.1	3561.0	8325.8	0.000
d ₉₀	188438.4	62812.8	3274.6	0.000
Span	0.63	0.21	60.4	0.000

Table C2-5. Tukey's pairwise comparison test for the examination of sources of statistical differences found in one-way ANOVA for the four shredding programs of secondary shredding applied in SRF

Shredding program	p-value for variable d ₁₀			p-value for variable d ₅₀			p-value for variable d ₉₀			p-value for variable span		
P2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
P4	0.000		0.000	0.000		0.000	0.000		0.000	0.000		0.000
P5	0.000	0.000		0.004	0.000	0.000		0.000	0.000		0.000	0.000
P9	0.000	0.000	0.004		0.000	0.000	0.000		0.000	0.000	0.000	

C3. ToS-based calculations for the construction of nomographs

Table C3- 1. Calculations of fundamental error (FE) during sub-sampling for the determination of Total [Cl] in SRF with the use of ToS formula under three shredding scenarios: *current sub-sampling plan* (including both primary and secondary shredding); *sub-sampling without secondary shredding* (only use of primary shredding); and *sub-sampling without shredding*

Current sub-sampling					Sub-sampling without secondary shredding					Sub-sampling without shredding				
M _s [g]	d [cm]	C ¹	s _{FE} ²	FE (%) ³	M _s [g]	d [cm]	C ¹	s _{FE} ²	FE (%) ³	M _s [g]	d [cm]	C ¹	s _{FE} ²	FE (%) ³
850.0	3	1.8	-	-	850.0	3	1.8	-	-	850.0	3	1.8	-	-
425.0	3	1.8	0.057	23.9	425.0	3	1.8	0.057	23.9	425.0	3	1.8	0.057	23.9
425.0	0.4	5.8	0.000	0.0	425.0	0.4	5.8	0.000	0.0	212.5	3	1.8	0.114	33.8
212.5	0.4	5.8	0.001	3.0	212.5	0.4	5.8	0.001	3.0	106.3	3	1.8	0.229	47.8
106.3	0.4	5.8	0.002	4.2	106.3	0.4	5.8	0.002	4.2	53.1	3	1.8	0.457	67.6
53.1	0.4	5.8	0.003	5.9	53.1	0.4	5.8	0.003	5.9	26.6	3	1.8	0.915	95.7
26.6	0.4	5.8	0.007	8.4	26.6	0.4	5.8	0.007	8.4	13.3	3	1.8	1.830	135.3
13.3	0.4	5.8	0.014	11.8	13.3	0.4	5.8	0.014	11.8	6.6	3	1.8	3.659	191.3
6.6	0.4	5.8	0.028	16.7	6.6	0.4	5.8	0.028	16.7	0.3	3	1.8	154.7	1243.7
6.6	0.015	7.2	0.000	0.0	0.3	0.4	5.8	1.181	108.7					
0.3	0.015	7.2	0.000	0.9										
Overall FE (%)⁴				33.6					113.7					1272.6

¹The sampling constant, C, derived from **Eq. 2-4**, changes after shredding due to the alteration of physical characteristics of the sample; ²Derived from **Eq. 2-3** using as M_L the sample mass at the previous sub-sampling point and as M_s the sub-sample mass at the related sub-sampling point; ³Derived from the square root of **Eq. 2-3**; ⁴Derived from the square root of the sum of the variances, s_{FE}², at each stage of sub-sampling

C4. ANOVA results and diagnostic checking for the moisture evaporation during shredding

Table C4- 2. Residual moisture content in three SRF test sub-samples at three different stages of shredding: before primary shredding (with cutting mill), after primary shredding/ before secondary shredding, after secondary shredding (with cryomill).

Test sub-sample	Residual moisture (% w/w)	Stages of shredding
1	1.94	Before primary shredding
	2.23	Before primary shredding
	1.33	Before primary shredding
	1.80	Before primary shredding
	2.66	Before primary shredding
	1.03	Before primary shredding
2	1.85	After primary shredding/ Before secondary shredding
	1.51	After primary shredding/ Before secondary shredding
	1.50	After primary shredding/ Before secondary shredding
	2.45	After primary shredding/ Before secondary shredding
	1.72	After primary shredding/ Before secondary shredding
	1.97	After primary shredding/ Before secondary shredding
3	1.82	After secondary shredding
	1.83	After secondary shredding
	1.85	After secondary shredding
	1.87	After secondary shredding
	2.03	After secondary shredding
	2.02	After secondary shredding

Table C4- 2. Key assumptions need to be met for the conduction of one-way ANOVA at a significance level $\alpha=0.05$ for the examination of statistical difference among shredding processes regarding the residual MC in SRF: Assumptions are fulfilled.

Test	Aspect of examination	p-value
Raw data	Normal distribution	0.80
Residuals	Normal distribution	0.76
Levene's test	Homogeneity of variance	0.05
ANOVA	Test of significance	0.94

APPENDIX D: Statistical quantification of sub-sampling uncertainty and comparison with ToS for critical SRF properties

D1. Knowledge background on nested-ANOVA

Herein, the related mathematical formulas for a four-level nested-ANOVA are provided so that to cover the necessary background for both nested designs: *Gross_nested* which corresponds to four level and *Intra_nested* which corresponds to three level.

In the four-level nested-ANOVA, there are four F-statistics, one for each level. In general, the F-statistic at each level is the ratio of mean square at this level by the mean square at the level immediately below it. After the calculation of F-statistic at each level, the F-critical value from the F-distribution is calculated for each level having, the total number of groups in that level minus the number of groups at the higher level as degrees of freedom in the numerator and the number of sub-groups at the lower level minus the number of groups at that level as degrees of freedom in the denominator. Finally, it is examined the following assumptions:

- If **F-statistic** > **F-critical** , then the variation is significant
- If **F-statistic** < **F-critical** , then the difference is not significant

The model for the general four stage nested design is (Montgomery, 2017):

$$Y_{i,j,k,l,m} = \mu + \tau_i + \beta_{j(i)} + \gamma_{k(ij)} + \delta_{l(ijk)} + \varepsilon_{(ijkl)m} \quad \left\{ \begin{array}{l} i = 1, 2, \dots, a \\ j = 1, 2, \dots, b \\ k = 1, 2, \dots, c \\ l = 1, 2, \dots, d \\ m = 1, 2, \dots, n \end{array} \right. \quad \text{Eq. D1-1}$$

where, μ is the overall mean, τ_i is “effect” of the first level of sampling, $\beta_{j(i)}$ is the “effect” of the second level of sampling, $\gamma_{k(ij)}$ is the “effect” of the third level of sampling, $\delta_{l(ijk)}$ is the “effect” of the fourth level of sampling and $\varepsilon_{(ijkl)m}$ is the random error. In Table B-1, the mathematical formulas for

the calculation of sum of square (SS) and variance of components for four-level nested-ANOVA are presented.

Table D1-1. Mathematical formulas for the calculation of sum of squares and variance components for four-level nested-ANOVA.

Source of Variation	Sum of Squares (SS)	df	Mean Square (MS)	F	Variance components
1 st stage (within SRF)	$bcdn \sum_i (\bar{y}_{i...} - \bar{y}....)^2$	a-1 (a=2)	$\frac{SS_{1st\ stage}}{a-1}$	$\frac{MS_{1st}}{MS_{2nd}}$	$\frac{MS_{1st} - MS_{2nd}}{bcdn}$
2 st stage (within groups A and B)	$cdn \sum_i \sum_j (\bar{y}_{ij...} - \bar{y}_i....)^2$	a(b-1) (b=2)	$\frac{SS_{2st\ stage}}{a(b-1)}$	$\frac{MS_{2nd}}{MS_{3rd}}$	$\frac{MS_{2nd} - MS_{3rd}}{cdn}$
3 rd stage (within groups A1, A2, etc.)	$dn \sum_i \sum_j \sum_k (\bar{y}_{ijk...} - \bar{y}_{ij...})^2$	ab(c-1) (c=2)	$\frac{SS_{3rd\ stage}}{ab(c-1)}$	$\frac{MS_{3rd}}{MS_{4th}}$	$\frac{MS_{3rd} - MS_{4th}}{dn}$
4 th stage (within groups A11, A12, etc.)	$n \sum_i \sum_j \sum_k \sum_l (\bar{y}_{ijkl...} - \bar{y}_{ijk...})^2$	abc(d-1) (d=2)	$\frac{SS_{4th\ stage}}{abc(d-1)}$	$\frac{MS_{4th}}{MS_{within}}$	$\frac{MS_{4th} - MS_{within}}{n}$
Error (within groups A111, A112, etc.)	$\sum_i \sum_j \sum_k \sum_l \sum_m (\bar{y}_{ijklm} - \bar{y}_{ijkl...})^2$	abcd(n-1) (n=3)	$\frac{SS_{within}}{abcd(n-1)}$		MS_{within}
Total	$\sum_i \sum_j \sum_k \sum_l \sum_m (y_{ijklm} - \bar{y}....)^2$	abcdn-1	$\frac{SS_{total}}{abcdn-1}$		$s_{error}^2 + s_{4th}^2 + s_{3rd}^2 + s_{2nd}^2 + s_{1st}^2$

The variances from the final column provide the variance of each stage of sub-sampling and the square root of these variances provide the uncertainty at each stage of sub-sampling. In addition, the ratio of each variance to the total variance expresses the contribution of each stage of sampling to the overall variation.

D2. Datasets used for nested-ANOVA for the quantification of sub-sampling uncertainty for all SRF properties: moisture, ash, NCV, and Cl

Table D2-1. Analytical results of SRF critical properties – Total [Cl], moisture (MC), ash, and caloric content (NCV) – for the calculation of sub-sampling uncertainty emerging from the 1st to 4th stage of sub-sampling through four level nested-ANOVA (*Gross_nested*: from the sample mass of nearly 850 g to the sub-sample of 53 g) .

No.	SRF properties				Sub-sampling stages in <i>Gross_nested</i> design			
	Total [Cl] (% w/w _d)	MC (% w/w)	NCV (MJ kg _d ⁻¹)	Ash (% w/w _d)	1st	2nd	3rd	4th
1	1.18	16.81	23.41	13.26	A	A1	A11	A111
2	0.99	16.89	23.26	13.38	A	A1	A11	A111
3	0.93	17.04	22.89	12.95	A	A1	A11	A111
4	0.94	16.52	23.67	12.96	A	A1	A11	A112
5	1.06	16.58	23.54	13.31	A	A1	A11	A112
6	0.94	16.49	24.15	12.84	A	A1	A11	A112
7	1.16	16.40	24.32	13.96	A	A1	A12	A121
8	1.12	16.55	23.60	13.55	A	A1	A12	A121
9	1.13	16.46	23.60	13.46	A	A1	A12	A121
10	1.29	16.70	24.11	13.00	A	A1	A12	A122
11	1.48	16.92	24.26	13.27	A	A1	A12	A122
12	1.29	16.67	23.93	13.28	A	A1	A12	A122
13	0.98	17.04	24.08	12.85	A	A2	A21	A211
14	0.98	17.17	23.89	12.65	A	A2	A21	A211
15	0.89	16.98	24.34	12.93	A	A2	A21	A211
16	1.03	16.99	23.23	13.27	A	A2	A21	A212
17	1.10	16.88	23.07	12.81	A	A2	A21	A212
18	1.02	16.85	23.26	12.93	A	A2	A21	A212
19	1.34	16.74	24.22	13.28	A	A2	A22	A221
20	1.17	16.71	24.52	13.61	A	A2	A22	A221
21	1.30	16.66	24.32	13.72	A	A2	A22	A221
22	1.09	16.50	23.67	13.97	A	A2	A22	A222
23	1.00	16.65	23.20	13.78	A	A2	A22	A222
24	1.09	16.43	23.72	13.99	A	A2	A22	A222
25	0.89	16.81	23.69	13.95	B	B1	B11	B111
26	0.97	16.77	23.68	14.35	B	B1	B11	B111
27	1.01	16.81	23.32	14.28	B	B1	B11	B111
28	1.17	16.75	24.86	13.62	B	B1	B11	B112
29	1.14	16.75	24.81	13.61	B	B1	B11	B112
30	1.19	16.69	24.24	13.84	B	B1	B11	B112
31	1.11	16.67	23.18	13.56	B	B1	B12	B121
32	1.09	16.62	23.47	13.89	B	B1	B12	B121
33	1.21	16.48	22.52	13.98	B	B1	B12	B121
34	1.11	16.45	22.40	13.57	B	B1	B12	B122
35	1.08	16.52	22.72	13.49	B	B1	B12	B122
36	1.17	16.49	23.03	13.72	B	B1	B12	B122
37	0.90	17.06	23.54	13.84	B	B2	B21	B211

SRF properties					Sub-sampling stages in Gross_nested design			
No.	Total [Cl] (% w/w _d)	MC (% w/w)	NCV (MJ kg _d ⁻¹)	Ash (% w/w _d)	1st	2nd	3rd	4th
38	0.97	16.85	23.71	13.48	B	B2	B21	B211
39	0.93	16.78	23.41	13.83	B	B2	B21	B211
40	0.89	16.51	23.22	13.19	B	B2	B21	B212
41	0.93	16.49	23.57	12.93	B	B2	B21	B212
42	0.84	16.45	23.16	12.94	B	B2	B21	B212
43	0.92	16.44	22.34	13.86	B	B2	B22	B221
44	1.04	16.29	22.23	13.51	B	B2	B22	B221
45	0.99	16.26	21.95	14.03	B	B2	B22	B221
46	0.93	16.39	23.32	13.59	B	B2	B22	B222
47	0.99	16.25	23.06	13.13	B	B2	B22	B222
48	0.95	16.24	23.48	13.22	B	B2	B22	B222

Table D2-2. Analytical results of SRF critical properties – Total [Cl], moisture (MC), ash, and caloric content (NCV) – for the calculation of sub-sampling uncertainty emerging from the 5th to 7th stage of sub-sampling through three level nested-ANOVA (*Intra_nested*: from the sub-sample mass of nearly 53 g to the test sub-sample of 6-7 g) .

SRF properties					Sub-sampling stages in Intra_nested design		
No.	Total [Cl] (% w/w _d)	MC (% w/w)	NCV (MJ kg _d ⁻¹)	Ash (% w/w _d)	5 th	6 th	7 th
1	1.60	16.34	24.52	13.69	a	a1	a11
2	1.63	16.15	24.39	13.15	a	a1	a11
3	1.47	16.05	25.30	13.23	a	a1	a11
4	1.41	15.94	24.43	12.94	a	a1	a12
5	1.56	15.82	23.87	13.36	a	a1	a12
6	1.48	15.87	24.44	13.07	a	a1	a12
7	1.37	15.79	24.78	13.34	a	a2	a21
8	1.38	15.89	24.22	13.76	a	a2	a21
9	1.25	15.71	23.75	13.45	a	a2	a21
10	1.38	15.68	23.64	13.93	a	a2	a22
11	1.40	15.60	23.04	13.98	a	a2	a22
12	1.49	15.59	23.15	14.32	a	a2	a22
13	1.05	16.68	23.66	12.84	b	b1	b11
14	1.12	16.40	23.53	13.02	b	b1	b11
15	1.09	16.17	23.44	13.35	b	b1	b11
16	1.28	16.34	24.16	13.41	b	b1	b12
17	1.32	16.22	23.68	13.89	b	b1	b12
18	1.30	16.23	24.26	13.79	b	b1	b12
19	1.51	16.10	24.45	13.15	b	b2	b21
20	1.48	16.26	23.45	12.72	b	b2	b21
21	1.53	16.06	24.27	13.06	b	b2	b21
22	1.29	16.08	22.71	12.19	b	b2	b22
23	1.27	16.03	23.52	11.89	b	b2	b22
24	1.33	16.21	23.34	12.11	b	b2	b22

D3. Diagnostic checking of nested-ANOVA for the quantification of sub-sampling uncertainty for all SRF properties: moisture, ash, NCV, and Cl

The goodness-of-fit of the datasets of SRF properties to the normal distribution were checked for both designs (*Gross_nested* and *Intra_nested*) by using the Anderson-Darling test (**Table D3-1**).

According to the analysis, p -values were higher than 0.05 indicating that data follow normal distribution (using 0.05 as the critical significance level). The normality of residuals was also checked indicating that the assumption III is fulfilled (**Table D3-1**).

Table D3-1. Anderson Darling test for examination of normal distribution of data and residuals (significance level $\alpha=0.05$) – Examination of I and III requirements of ANOVA.

SRF properties	<i>Gross_nested</i> design		<i>Intra_nested</i> design	
	p -value	p -value	p -value	p -value
	Raw data*	Residuals**	Raw data*	Residuals**
MC (% w/w)	0.89	0.59	0.99	0.62
Ash (% w/w _d)	0.77	0.46	0.87	0.87
Cl (% w/w _d)	0.53	0.92	0.96	0.98
NCV (MJ/kg _d)	0.87	0.72	0.92	0.94

* p -values of raw data - experimental results (if $p > 0.05$ then normal distribution is assumed); ** p -values of residuals obtained from nested-ANOVA (if $p > 0.05$ then normal distribution is assumed)

In relation to the assumption IV, tests showed that there is HOV at a significance level 0.01, but there is heterogeneity in some stages of sub-sampling process when the alpha value was 0.05 (**Table D3-2**).

For example, Levene's test showed that the p -values of Total [Cl] at the 2nd, 3rd and 4th stage of sub-sampling process are less than 0.05 but greater than 0.01. In addition, heterogeneity of variance was detected by Levene's test in case of MC in the 3rd stage of sub-sampling ($p < 0.01$) but Cochran's C test showed HOV at a significance level of 0.01.

Thus, the key requirements were mostly fulfilled concluding that the results of nested ANOVA can be used for the quantification of the uncertainty introduced during the sub-sampling for the quality characterization of SRF.

Table D3-2. Examination of homogeneity of variance (HOV) for the several levels of nested ANOVA (stages of sub-sampling) using both Levene's and Cochran's C test at a significance level $\alpha = 0.05$ – Examination of IV requirement of ANOVA

Sub-sampling stages	<i>Gross_nested design</i>				<i>Intra_nested design</i>				<i>Gross_nested design</i>				<i>Intra_nested design</i>			
	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th		1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	
<i>p</i> -value – Levene's test								<i>p</i> -value – Cochran's C test								
MC (% w.t)	0.98	0.28	0.01	0.05	0.40	0.34	0.21		0.96	0.19	0.01	0.55	0.47	0.30	0.41	
Ash (% w/w _d)	0.70	0.05	0.32	0.74	0.22	0.14	0.92		0.78	0.29	0.70	0.99	0.18	0.52	0.99	
Cl (% w/w _d)	0.24	0.03	0.01	0.02	0.45	0.03	0.12		0.13	0.04	0.05	0.61	0.25	0.73	0.48	
NCV (MJ kg _d ⁻¹)	0.15	0.16	0.02	0.20	0.29	0.47	0.35		0.02	0.12	0.55	0.94	0.36	0.49	0.77	

D4. ToS-based calculations of fundamental errors for all SRF properties: moisture, ash, NCV, and CI

The calculation of sampling factor (**Eq. 2-4**) was calculated following the steps described in **Section 4.2.3**. The concentration of the analyte used for the calculation of the compositional factor (**Eq. 2-5**) derived from the average concentration of *Gross_nested* and *Intra_nested* design. Table **D4-1** presents the values of sampling factor selected for the theoretical calculation of minimum sub-sampling uncertainty (FE) for the determination of critical SRF parameters. In Table **D4-2**, the calculations along with the minimum uncertainty arising from each stage of sub-sampling (FE) for the determination of moisture, ash and CI content in SRF is presented.

Table D4-1. Sampling factor, C, after each stage of shredding based on physical characteristics of SRF for the selected fuel properties for the calculation of FE following the ToS-formula.

Shredding stages	C for <i>Gross_nested</i> ¹			C for <i>Intra_nested</i> ¹		
	MC	Ash	Total [CI]	MC	Ash	Total [CI]
Before shredding	0.05	0.16	1.8	0.06	0.16	1.4
After Cutting Mill	0.17	0.51	5.8	0.18	0.52	4.5
After CryoMill*	-	-	7.2	-	-	5.6

¹ The values of C are different for the two nested designs as the concentration of the analytes (arithmetic mean that derives from analytical values of 16 and 8 sub-samples for *Gross_nested* and *Intra_nested*, respectively) affect the compositional factor; *Cryogenic shredding (CryoMill) was applied in the sub-samples only for the determination of Total [CI] and NCV; For NCV, values were not obtained as ToS considers analytes as contaminants

Table D4-2. Minimum sub-sampling uncertainty arising from each sub-sampling stage only due to constitutional heterogeneity (FE) for determination of SRF properties based on ToS formula: moisture content (MC), ash, and Total [Cl].

Sub-sampling points ¹	Sub-sampling plan ²		MC				Ash				Total [Cl]					
			<i>Gross_nested</i>		<i>Intra_nested</i>		<i>Gross_nested</i>		<i>Intra_nested</i>		<i>Gross_nested</i>		<i>Intra_nested</i>		<i>Gross_nested</i>	
	d [cm]	M _s [g]	C*	FE (%) ⁴	C*	FE (%) ⁴	C*	FE (%) ⁴	C*	FE (%) ⁴	d [cm]	M _s [g]	C*	FE (%) [*]	C*	FE (%) ⁴
A	3.00	850	0.05		0.06		0.16		0.16		3.00	850	1.82		1.39	
B	3.00	425	0.05	4.1	0.06	4.2	0.16	7.1	0.16	7.16	3.00	425	1.82	23.8	1.39	20.9
C	0.40	425	0.17	0.0	0.18	0.0	0.51	0.0	0.52	0.00	0.40	425	5.82	0.0	4.46	0.0
D	0.40	213	0.17	0.5	0.18	0.5	0.51	0.9	0.52	0.88	0.40	213	5.82	2.9	4.46	2.6
E	0.40	106	0.17	0.7	0.18	0.7	0.51	1.2	0.52	1.25	0.40	106	5.82	4.1	4.46	3.6
F	0.40	53	0.17	1.0	0.18	1.0	0.51	1.8	0.52	1.76	0.40	53	5.82	5.9	4.46	5.1
G	0.40	27	0.17	1.4	0.18	1.5	0.51	2.5	0.52	2.50	0.40	27	5.82	8.3	4.46	7.3
H	0.40	13	0.17	2.0	0.18	2.1	0.51	3.5	0.52	3.53	0.40	13	5.82	11.7	4.46	10.3
I	0.40	7	0.17	2.9	0.18	2.9	0.51	4.9	0.52	4.99	0.40	7	5.82	16.6	4.46	14.5
J	0.40	1-1.4	0.17	7.9	0.18	8.1	0.51	16.6	0.52	16.77	0.015	7	7.27	0.0	5.58	0.0
K											0.015	0.3	7.27	0.9	5.58	0.8
Total FE (%)⁵			9.8		10		19.3		19.5				33.3		29.2	

¹Each sub-sampling point refers to a specific mass and particle size of the sub-sample, the movement from one point to another indicate the stages of riffle splitting and shredding; ²The sub-sampling plans (the stages of mass and particle size reduction) for the determination of MC and ash were identical with an analytical portion ca. 1g; ³The sub-sampling plan for the determination of Total [Cl] was slightly different: further particle size reduction took place with CryoMill and the analytical portion was ca. 0.3g; ⁴FE was expressed as % relative standard deviation and calculated from the square root of **Eq. 2-3**; ⁵Derived from the square root of the sum of the s_{FE}^2 at each sub-sampling stage – the average of total FE between *Gross_nested* and *Intra_nested* designs used for the comparison with the statistical results; *the sampling constant, C: is different amongst the analytes due to their different fractions in the sample and changes after each stage of shredding due to the alteration of physical characteristics of the sample (Pitard, 1993)

D5. Post hoc test of nested-ANOVA

Tukey test were carried out (**Table D5-1**) showing that there is statistical difference between sub-samples within sample at each sub-sampling stage for all analytes with an exception being the MC and NCV at the 7th stage and Ash in the 2nd and 3rd stage.

However, the significance test of nested-ANOVA showed in **Table 5-16** indicated that there was at least one pair of nested sub-samples which were statistically different to each other only in the last stages of both designs: 4th (*Gross_nested*) and 7th (*Intra_nested*). A disagreement between ANOVA significance test and post hoc test might presage a false alarm of significant difference (Tian et al., 2018).

Table D5-1. Tukey test for examination of sources of statistical differences found in nested-ANOVA for each sub-sampling stage for the determination of SRF properties.

SRF properties	<i>Gross_nested</i> design				<i>Intra_nested</i> design		
	1st stage	2nd stage	3rd Stage	4th stage	5th stage	6th stage	7th stage
MC (% w/w)	$\bar{X}_A \neq \bar{X}_B$	$\bar{X}_{A1} \neq \bar{X}_{A2}$ AND $\bar{X}_{B1} \neq \bar{X}_{B2}$	$\bar{X}_{A21} \neq \bar{X}_{A22}$ AND $\bar{X}_{B11} \neq \bar{X}_{B12}$ AND $\bar{X}_{B21} \neq \bar{X}_{B22}$	$\bar{X}_{A111} \neq \bar{X}_{A112}$ AND $\bar{X}_{A121} \neq \bar{X}_{A122}$ AND $\bar{X}_{B211} \neq \bar{X}_{B212}$	$\bar{X}_a \neq \bar{X}_b$	$\bar{X}_{a1} \neq \bar{X}_{a2}$ AND $\bar{X}_{b1} \neq \bar{X}_{b2}$	ND*
Ash (% w/w _d)	$\bar{X}_A \neq \bar{X}_B$	ND*	ND*	$\bar{X}_{A221} \neq \bar{X}_{A222}$ AND $\bar{X}_{B111} \neq \bar{X}_{B112}$	$\bar{X}_a \neq \bar{X}_b$	$\bar{X}_{a1} \neq \bar{X}_{a2}$ AND $\bar{X}_{b1} \neq \bar{X}_{b2}$	$\bar{X}_{b21} \neq \bar{X}_{b22}$
Cl (% w/w _d)	$\bar{X}_A \neq \bar{X}_B$	$\bar{X}_{B1} \neq \bar{X}_{B2}$	$\bar{X}_{A11} \neq \bar{X}_{A12}$ AND $\bar{X}_{A21} \neq \bar{X}_{A22}$	$\bar{X}_{A121} \neq \bar{X}_{A122}$ AND $\bar{X}_{A221} \neq \bar{X}_{A222}$ AND $\bar{X}_{B111} \neq \bar{X}_{B112}$	$\bar{X}_a \neq \bar{X}_b$	$\bar{X}_{a1} \neq \bar{X}_{a2}$ AND $\bar{X}_{b1} \neq \bar{X}_{b2}$	$\bar{X}_{b11} \neq \bar{X}_{b12}$ AND $\bar{X}_{b21} \neq \bar{X}_{b22}$
NCV (MJ kg_d⁻¹)	$\bar{X}_A \neq \bar{X}_B$	$\bar{X}_{B1} \neq \bar{X}_{B2}$	$\bar{X}_{B11} \neq \bar{X}_{B12}$ AND $\bar{X}_{B21} \neq \bar{X}_{B22}$	$\bar{X}_{A211} \neq \bar{X}_{A212}$ AND $\bar{X}_{B111} \neq \bar{X}_{B112}$ AND $\bar{X}_{B221} \neq \bar{X}_{B222}$	$\bar{X}_a \neq \bar{X}_b$	$\bar{X}_{a1} \neq \bar{X}_{a2}$	ND*

ND: No statistical difference was detected between samples

APPENDIX E: Statistical quantification of sub-sampling uncertainty for TG-DTG

E1. Diagnostic results of PCA for 37 critical points from TG-DTG curve

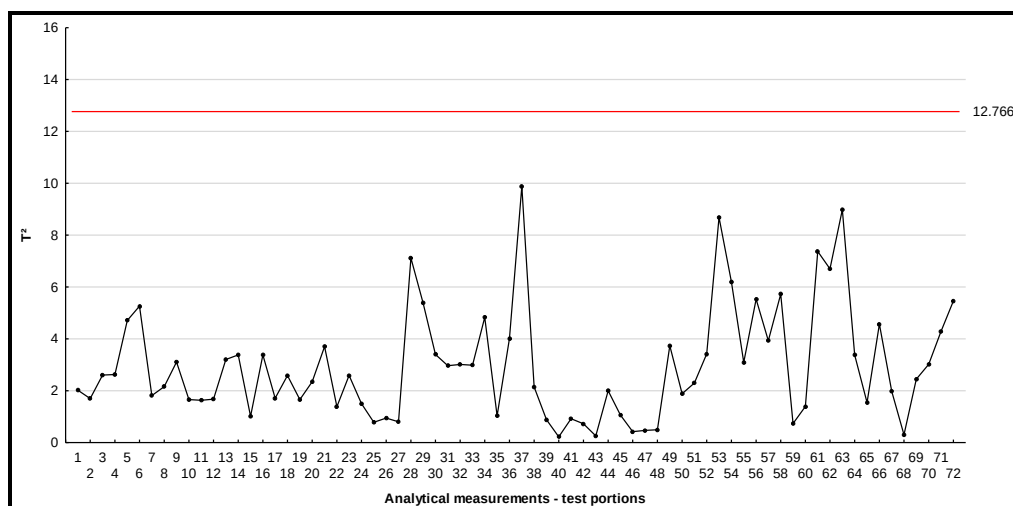


Figure E1-1. Hotelling T^2 control chart for the detection of outliers obtained from 72 measurements of TG-DTG for SRF sample including both *Gross-nested* (16 sub-samples with 3 replicate measurements) and *Intra-nested* (8 sub-samples with 3 replicate measurements) design. Points above the red line indicate outlier values: No outliers detected.

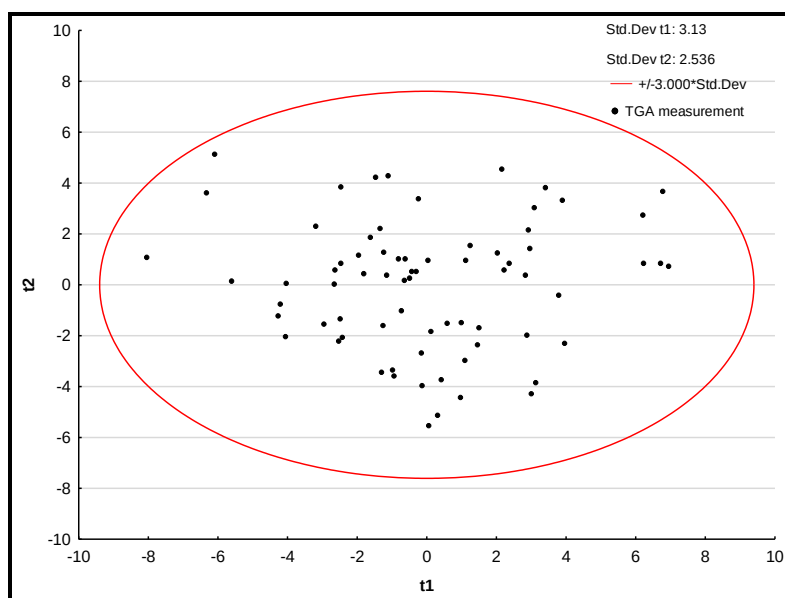


Figure E1-2. Scatterplot of x-scores (transformed values of X observations – TG-DTG measurements in the PCA system) for the detection of outliers obtained from 72 measurements of TG-DTG for SRF sample including both *Gross-nested* and *Intra-nested* design. Points out of the red circle (± 3 standard deviation) indicate outlier values: No outliers detected.

E2. PCA: loading values of critical points from TG-DTG curve

Table E2-1. PCA loadings: normalised raw data. Variables with loading values ≥ 0.60 considered sufficiently influential in determining the corresponding principal component (PC): PC1 includes 13 variables with number 1, 2, 3, 5, 9, 15, 16, 17, 24, 29, 30, 32 and 33; PC2 includes 6 variables with number 4, 10, 12, 24, 25 and 26; PC3 includes 7 variables with number 6, 18, 19, 20, 23, 34 and 36; PC4 includes only one variable with number 22.

Variable number	Variable name	PC 1	PC 2	PC 3	PC 4
1	T _{10%}	0.70	-0.33	0.21	0.18
2	T _{20%}	0.76	-0.17	-0.03	0.45
3	T _{30%}	0.88	0.00	-0.09	0.37
4	T _{50%}	0.56	0.72	-0.03	-0.16
5	T _{75%}	0.87	0.40	-0.04	-0.09
6	Res.MC	-0.24	-0.28	-0.76	0.07
7	Res.MC_Inf.T	0.03	0.11	0.07	-0.09
8	Res.MC_Mid.T	-0.18	-0.57	0.21	0.28
9	1st_ML	-0.66	0.15	-0.09	-0.13
10	1st_Inf.T	0.57	-0.62	0.03	-0.43
11	1st_Mid.T	0.55	-0.59	-0.04	-0.41
12	2nd_ML	-0.14	-0.88	-0.01	-0.02
13	2nd_Inf.T	0.38	-0.47	-0.46	0.23
14	2nd_Mid.T	0.55	-0.20	0.27	0.59
15	3rd_ML	0.65	0.38	-0.16	-0.26
16	3rd_Inf.T	0.79	0.39	-0.03	-0.08
17	3rd_Mid.T	0.89	0.27	0.01	-0.09
18	4th_ML	0.17	0.05	-0.73	0.25
19	4th_Inf.T	0.08	0.11	-0.69	-0.37
20	4th_Mid.T	-0.08	0.21	-0.75	-0.11
21	Res.	-0.21	0.49	0.42	0.21
22	1st_RML	0.06	-0.58	0.26	-0.62
23	1st_On.T	0.31	-0.45	0.67	-0.09
24	1st_Peak.T	0.61	-0.62	0.00	-0.43
25	1st_End.T	0.56	-0.61	-0.05	-0.43
26	2nd_RML	-0.44	-0.67	-0.23	0.18
27	2nd_On.T	0.31	-0.38	-0.57	0.17
28	2nd_Peak.T	0.42	-0.58	-0.37	0.37
29	2nd_End.T	0.64	-0.21	0.37	0.30
30	3rd_RML	-0.65	-0.09	-0.30	-0.11

Variable number	Variable name	PC 1	PC 2	PC 3	PC 4
31	3rd_On.T	0.46	0.14	-0.14	0.02
32	3rd_Peak.T	0.73	0.47	-0.07	-0.09
33	3rd_End.T	0.69	0.45	0.01	-0.14
34	4th_RML	0.19	-0.02	-0.60	0.45
35	4th_On.T	0.01	0.09	-0.32	-0.33
36	4th_Peak.T	0.01	0.11	-0.64	-0.18
37	4th_End.T	0.02	-0.03	0.04	0.39

E3. Diagnostic checking of nested-ANOVA for the quantification of sub-sampling uncertainty for TG-DTG of SRF

Table E3-1 shows that data follow the normal distribution for all critical points in both designs excluding variables 36 and 37 for both designs, variable 19 for *Gross_nested* design and variable 23 for *Intra_nested* design. **Table E3-1** shows that residuals follow the normal distribution with only exception being variable 7 for *Gross_nested* design, which was not captured by any PC. **Table E3-2** shows that the assumption of HOV is violated in many cases for the different stages of mass reduction – sub-sampling. Key required assumptions for both balanced nested design are mostly met and therefore results from nested-ANOVA can be used for the quantification of the uncertainty arising from the sub-sampling for TG-DTG of SRF.

Table E3-1. Anderson Darling test for examination of normal distribution of raw data and residuals (significance level: $\alpha=0.05$) – Examination of I and III requirements of ANOVA.

Variable number	Critical points of TG-DTG curve	Gross_nested design		Intra_nested design	
		p-value	p-value	p-value	p-value
		Raw data*	Residuals**	Raw data*	Residuals**
1	T _{10%}	0.29	0.14	0.99	0.98
2	T _{20%}	0.99	0.56	0.19	0.92
3	T _{30%}	0.50	0.97	0.24	0.99
4	T _{50%}	0.18	0.95	0.79	0.99
5	T _{75%}	0.13	0.41	0.47	0.83
6	Res.MC	0.10	0.06	0.94	0.82
7	Res.MC_Inf.T	0.00	0.04	0.02	0.24
8	Res.MC_Mid.T	0.11	0.51	0.55	0.49
9	1st_ML	0.39	0.8	0.93	0.98
10	1st_Inf.T	0.61	0.64	0.19	0.73
11	1st_Mid.T	0.39	0.05	0.70	0.36
12	2nd_ML	0.83	0.94	0.93	0.83
13	2nd_Inf.T	0.55	0.97	0.93	0.97
14	2nd_Mid.T	0.75	0.72	0.64	0.99
15	3rd_ML	0.21	0.99	0.87	0.92
16	3rd_Inf.T	0.89	0.9	0.73	0.81
17	3rd_Mid.T	0.70	0.42	0.99	0.88

Variable number	Critical points of TG-DTG curve	Gross_nested design		Intra_nested design	
		p-value	p-value	p-value	p-value
		Raw data*	Residuals**	Raw data*	Residuals**
18	4th_ML	0.99	0.76	0.43	0.59
19	4th_Inf.T	0.04	0.05	0.22	0.89
20	4th_Mid.T	0.63	0.22	0.67	0.92
21	Res.	0.40	0.16	0.27	0.69
22	1st_RML	0.27	0.48	0.58	0.55
23	1st_On.T	0.08	0.33	0.00	0.14
24	1st_Peak.T	0.45	0.13	0.89	0.98
25	1st_End.T	0.49	0.18	0.42	0.95
26	2nd_RML	0.46	0.95	0.87	0.97
27	2nd_On.T	0.06	0.79	0.80	0.92
28	2nd_Peak.T	0.79	0.98	0.98	0.53
29	2nd_End.T	0.91	0.69	0.26	0.99
30	3rd_RML	0.70	0.99	0.82	0.99
31	3rd_On.T	0.52	0.37	0.80	0.63
32	3rd_Peak.T	0.98	0.96	0.72	0.86
33	3rd_End.T	0.13	0.41	0.77	0.63
34	4th_RML	0.91	0.35	0.36	0.75
35	4th_On.T	0.08	0.94	0.01	0.2
36	4th_Peak.T	0.04	0.67	0.00	0.65
37	4th_End.T	0.00	0.11	0.02	0.5
38	S	0.63	0.85	0.97	0.97

* p -values of raw data – experimental results (if $p \geq 0.05$ then normal distribution is assumed); ** p -values of residuals after nested ANOVA (if $p \geq 0.05$ then normal distribution is assumed)

Table E3-2. Examination of homogeneity of variance (HOV) for the several levels of nested ANOVA (stages of sub-sampling) using both Levene's and Cochran's C test at a significance level: $\alpha = 0.05$ – Examination of IV requirement of ANOVA.

Sub-sampling stages	<i>Gross_nested design</i>							<i>Intra_nested design</i>						
	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th
Variables/ critical points of TG-DTG	<i>p-value – Levene's test</i>							<i>p-value – Cochran's C test</i>						
T _{10%}	0.03	0.20	0.00	0.00	0.26	0.91	0.17	0.012	0.06	0.00	0.00	0.27	0.94	0.74
T _{20%}	0.41	0.61	0.02	0.04	0.09	0.95	0.62	0.176	0.64	0.10	0.12	0.19	0.96	0.91
T _{30%}	0.43	0.32	0.00	0.02	0.04	0.30	0.24	0.312	0.54	0.09	0.32	0.05	0.54	0.04
T _{50%}	0.14	0.04	0.00	0.30	0.11	0.35	0.15	0.099	0.03	0.00	0.83	0.35	0.82	0.20
T _{75%}	0.17	0.02	0.00	0.05	0.59	0.83	0.37	0.281	0.02	0.00	0.66	0.49	0.94	0.51
Res.MC	0.03	0.03	0.03	0.00	0.82	0.33	0.01	0.001	0.00	0.00	0.00	0.68	0.36	0.17
Res.MC_Inf.T	0.08	0.02	0.00	0.00	0.08	0.16	0.00	0.000	0.00	0.00	0.00	0.03	0.00	0.00
Res.MC_Mid.T	0.34	0.08	0.00	0.00	0.58	0.20	0.00	0.496	0.01	0.00	0.00	0.58	0.54	0.01
1st_ML	0.11	0.16	0.00	0.00	0.77	0.69	0.48	0.142	0.03	0.00	0.01	0.66	0.85	0.85
1st_Inf.T	0.29	0.51	0.20	0.00	0.80	0.06	0.00	0.253	0.28	0.00	0.00	0.76	0.12	0.00
1st_Mid.T	0.76	0.52	0.06	0.00	0.64	0.15	0.07	0.178	0.13	0.00	0.00	0.32	0.24	0.04
2nd_ML	0.12	0.04	0.14	0.19	0.29	0.59	0.75	0.098	0.03	0.26	0.40	0.57	0.75	0.96
2nd_Inf.T	0.88	0.63	0.20	0.01	0.22	0.21	0.01	0.405	0.70	0.94	0.09	0.19	0.69	0.08
2nd_Mid.T	0.24	0.22	0.04	0.00	0.15	0.00	0.05	0.183	0.08	0.12	0.02	0.06	0.02	0.52
3rd_ML	0.50	0.01	0.00	0.20	0.05	0.19	0.13	0.306	0.04	0.00	0.66	0.18	0.66	0.37
3rd_Inf.T	0.29	0.78	0.56	0.13	0.79	0.13	0.06	0.328	0.95	0.89	0.79	0.87	0.47	0.22
3rd_Mid.T	0.42	0.42	0.00	0.13	0.24	0.42	0.11	0.419	0.52	0.22	0.55	0.18	0.57	0.31
4th_ML	0.18	0.07	0.11	0.01	0.23	0.21	0.07	0.073	0.06	0.04	0.03	0.43	0.09	0.41
4th_Inf.T	0.04	0.01	0.00	0.00	0.02	0.00	0.09	0.000	0.00	0.00	0.00	0.00	0.00	0.59
4th_Mid.T	0.03	0.24	0.07	0.00	0.84	0.38	0.03	0.048	0.35	0.27	0.00	0.82	0.30	0.13
Res.	0.34	0.05	0.00	0.03	0.83	0.35	0.52	0.502	0.00	0.00	0.01	0.63	0.19	0.93
1st_RML	0.53	0.51	0.08	0.00	0.84	0.09	0.09	0.308	0.49	0.01	0.07	0.82	0.38	0.46
1st_On.T	0.64	0.40	0.03	0.00	0.12	0.01	0.00	0.158	0.07	0.00	0.00	0.00	0.00	0.00

Sub-sampling stages	<i>Gross_nested design</i>							<i>Intra_nested design</i>						
	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th
Variables/ critical points of TG-DTG	<i>p-value – Levene’s test</i>							<i>p-value – Cochran’s C test</i>						
1st_Peak.T	0.59	0.15	0.03	0.00	0.83	0.57	0.19	0.267	0.12	0.00	0.00	0.50	0.67	0.26
1st_End.T	0.61	0.39	0.01	0.00	0.22	0.38	0.03	0.555	0.28	0.00	0.00	0.74	0.72	0.06
2nd_RML	0.01	0.00	0.00	0.00	0.37	0.28	0.17	0.013	0.00	0.00	0.33	0.56	0.84	0.20
2nd_On.T	0.14	0.09	0.02	0.01	0.03	0.12	0.06	0.133	0.01	0.01	0.10	0.09	0.30	0.20
2nd_Peak.T	0.37	0.47	0.30	0.06	0.20	0.01	0.06	0.255	0.35	0.30	0.43	0.18	0.11	0.20
2nd_End.T	0.10	0.11	0.00	0.12	0.02	0.00	0.08	0.157	0.25	0.00	0.67	0.01	0.00	0.26
3rd_RML	0.09	0.63	0.11	0.00	0.97	0.98	0.08	0.114	0.50	0.02	0.21	0.98	0.85	0.54
3rd_On.T	0.10	0.48	0.42	0.00	0.50	0.38	0.07	0.004	0.06	0.09	0.02	0.48	0.24	0.04
3rd_Peak.T	0.33	0.85	0.81	0.03	0.82	0.30	0.22	0.363	0.93	0.99	0.27	0.91	0.58	0.60
3rd_End.T	0.06	0.26	0.13	0.00	0.73	0.44	0.02	0.021	0.08	0.04	0.02	0.25	0.21	0.16
4th_RML	0.76	0.09	0.00	0.00	0.10	0.14	0.63	0.634	0.01	0.00	0.00	0.38	0.24	0.88
4th_On.T	0.63	0.59	0.27	0.00	0.23	0.12	0.00	0.399	0.00	0.01	0.04	0.00	0.00	0.00
4th_Peak.T	0.92	0.42	0.15	0.00	0.04	0.00	0.00	0.860	0.18	0.53	0.72	0.00	0.00	0.00
4th_End.T	0.19	0.77	0.03	0.00	0.64	0.17	0.00	0.292	0.25	0.00	0.00	0.67	0.01	0.03
S	0.00	0.16	0.89	0.25	0.81	0.10	0.85	0.82	0.92	0.20	0.75	0.95	0.74	0.82

E4. Results of nested-ANOVA for quantification of sub-sampling uncertainty for TG-DTG of SRF

Table E4-1. Variance components of nested-ANOVA indicating the variance of critical TG-DTG points of SRF at each stage of sub-sampling process (stages of riffle splitting and analysis including sample preparation) grouped by principal components (PCs).

Variables/ critical TG- DTG points	Variance at each stage of sub-sampling									Total variance	Arithmetic mean**
	PCs	1st stage	2nd stage	3rd stage	4th stage	5th stage	6th stage	7th stage	Average AE*		
T _{10%}	PC1	0.60	0.00	0.00	1.92	0.00	1.68	0.45	0.74	5.38	257.09
T _{20%}	PC1	0.00	0.00	0.05	0.79	0.00	1.48	0.02	0.39	2.73	282.29
T _{30%}	PC1	0.00	0.00	0.00	1.42	0.00	1.25	0.31	0.40	3.38	297.41
T _{75%}	PC1	0.00	3.82	0.00	11.23	0.00	0.00	3.46	2.15	20.65	420.41
1st_ML	PC1	0.01	0.00	0.00	0.10	0.00	0.07	0.02	0.05	0.25	7.63
3rd_ML	PC1	0.00	0.26	0.00	0.83	0.01	0.00	0.30	0.36	1.75	30.01
3rd_Inf.T	PC1	0.00	5.49	0.00	3.92	0.00	0.00	8.79	11.39	29.59	430.25
3rd_Mid.T	PC1	0.00	2.08	0.00	5.24	0.00	0.19	3.26	2.16	12.94	427.51
1st_Peak.T ¹	PC1	12.84	0.91	0.00	3.43	0.00	0.90	0.44	1.38	19.90	238.66
2nd_End.T	PC1	0.64	0.00	0.00	8.51	0.00	0.00	19.32	2.27	30.74	347.03
3rd_RML	PC1	0.00	0.00	0.00	1.10	0.00	0.00	0.63	1.66	3.39	8.58
3rd_Peak.T	PC1	0.00	5.79	0.00	1.28	0.00	0.00	5.14	9.81	22.02	425.30
3rd_End.T	PC1	0.00	7.61	0.00	6.34	0.00	0.00	8.40	23.01	45.35	440.87
T _{50%}	PC2	0.00	5.34	0.00	8.56	6.19	0.00	3.92	3.22	27.24	335.88
1st_Inf.T	PC2	10.78	1.00	0.00	2.45	0.00	0.68	0.31	1.74	16.96	238.25
2nd_ML	PC2	0.34	0.48	0.00	0.25	1.17	0.00	0.61	0.40	3.25	43.39
1st_End.T	PC2	7.33	0.19	0.00	2.24	0.00	0.37	0.21	1.06	11.39	243.83
2nd_RML	PC2	0.00	0.03	0.00	0.07	0.08	0.00	0.07	0.02	0.27	6.22
1st_Peak.T ¹	PC2	12.84	0.91	0.00	3.43	0.00	0.90	0.44	1.38	19.90	238.66
Res.MC	PC3	0.00	0.03	0.00	0.03	0.01	0.00	0.01	0.02	0.09	2.57
4th_ML	PC3	0.02	0.00	0.00	0.02	0.00	0.03	0.00	0.01	0.08	3.08
4th_Inf.T	PC3	8.38	0.00	7.60	0.00	0.01	0.00	0.23	137.90	154.12	640.17
4th_Mid.T	PC3	0.03	0.10	0.00	2.48	0.00	1.45	0.00	1.65	5.71	628.19
1st_On.T	PC3	16.70	1.17	0.00	3.03	0.00	2.12	0.00	20.20	43.21	225.37
4th_RML	PC3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47
4th_Peak.T	PC3	0.00	2.59	0.00	2.04	0.00	0.34	1.91	6.09	12.97	636.43
1st_RML	PC4	0.14	0.00	0.01	0.00	0.00	0.00	0.02	0.02	0.19	3.11
Res.MC_Inf.T	n.a	0.09	0.00	2.62	0.00	0.03	0.00	0.00	5.96	8.70	43.04
Res.MC_Mid.T	n.a	0.00	0.00	0.00	0.26	0.00	0.08	0.57	0.28	1.18	56.17

Variables/ critical TG- DTG points	Variance at each stage of sub-sampling									Total variance	Arithmetic mean**
	PCs	1st stage	2nd stage	3rd stage	4th stage	5th stage	6th stage	7th stage	Average AE*		
1st_Mid.T	n.a	6.62	0.00	0.00	0.61	0.08	0.00	0.38	0.69	8.39	240.49
2nd_Inf.T	n.a	0.00	0.00	0.43	0.43	0.00	4.05	4.52	1.51	10.94	297.38
2nd_Mid.T	n.a	0.00	0.00	0.09	0.37	0.00	0.00	0.60	0.19	1.25	304.53
Res.	n.a	0.31	0.00	0.02	0.39	1.12	0.00	1.18	0.79	3.81	12.85
2nd_On.T	n.a	0.00	0.33	0.10	0.05	0.00	0.82	0.05	0.65	2.00	282.25
2nd_Peak.T	n.a	0.00	0.26	0.47	0.78	0.00	3.34	3.50	0.79	9.15	297.36
3rd_On.T	n.a	0.00	2.19	0.00	2.37	0.00	5.63	1.43	11.75	23.37	417.61
4th_On.T	n.a	0.64	0.00	57.68	0.00	0.00	0.00	217.57	831.64	1107.53	598.71
4th_End.T	n.a	0.00	9.84	10.78	0.00	0.00	0.00	0.00	180.95	201.57	663.89
S		0.00E+00	1.05E-16	0.00E+00	8.88E-16	0.00E+00	0.00E+00	3.70E-16	1.08E-15	2.44E-15	2.55E-07

* Analytical error derived from the average of analytical errors of *Gross_nested* and *Intra_nested* design; refers to the stage from test sub-sample to test portion and analysis; ** Arithmetic mean of variables (critical points of TG-DTG curve of SRF sample) derived from the average values of *Gross_nested* (16 sub-samples) and *Intra_nested* (8 sub-samples) design;

¹Variable is captured by both PC1 and PC2; n.a: not applied as loadings of these variables were < 0.60

Table E4-2. Relative standard deviation (RSD) obtained from variance of components of nested-ANOVA indicating the sub-sampling uncertainty of critical TG-DTG points of SRF at each stage of sub-sampling process (stages of riffle splitting and analysis including sample preparation) grouped by principal components (PCs).

Variables/ critical TG- DTG points	RSD (%) at each stage of sub-sampling								Average Total	
	PCs	1st stage	2nd stage	3rd stage	4th stage	5th stage	6th stage	7th stage	AE*	RSD (%)
T10%	PC1	0.30	0.00	0.00	0.54	0.00	0.50	0.26	0.33	0.90
T20%	PC1	0.00	0.00	0.08	0.32	0.00	0.43	0.05	0.22	0.59
T30%	PC1	0.00	0.00	0.00	0.40	0.00	0.38	0.19	0.21	0.62
T75%	PC1	0.00	0.47	0.00	0.80	0.00	0.00	0.44	0.35	1.08
1st_ML	PC1	1.32	0.00	0.00	4.13	0.00	3.60	1.90	2.87	6.57
3rd_ML	PC1	0.00	1.71	0.00	3.05	0.30	0.00	1.79	1.98	4.41
3rd_Inf.T	PC1	0.00	0.55	0.00	0.46	0.00	0.00	0.69	0.78	1.26
3rd_Mid.T	PC1	0.00	0.34	0.00	0.54	0.00	0.10	0.42	0.34	0.84
1st_Peak.T1	PC1	1.51	0.40	0.00	0.78	0.00	0.39	0.28	0.47	1.87
2nd_End.T	PC1	0.23	0.00	0.00	0.84	0.00	0.00	1.26	0.43	1.60
3rd_RML	PC1	0.00	0.00	0.00	12.04	0.00	0.00	9.49	15.13	21.45
3rd_Peak.T	PC1	0.00	0.56	0.00	0.26	0.00	0.00	0.52	0.72	1.09
3rd_End.T	PC1	0.00	0.63	0.00	0.57	0.00	0.00	0.66	1.09	1.53
T50%	PC2	0.00	0.69	0.00	0.87	0.73	0.00	0.58	0.53	1.55
1st_Inf.T	PC2	1.38	0.42	0.00	0.66	0.00	0.34	0.23	0.53	1.73
2nd_ML	PC2	1.31	1.57	0.00	1.14	2.58	0.00	1.86	1.45	4.16

Variables/ critical TG- DTG points	RSD (%) at each stage of sub-sampling								Average Total	
	PCs	1st stage	2nd stage	3rd stage	4th stage	5th stage	6th stage	7th stage	AE*	RSD (%)
1st_End.T	PC2	1.11	0.18	0.00	0.62	0.00	0.25	0.19	0.39	1.38
2nd_RML	PC2	0.00	2.78	0.00	4.08	4.93	0.00	4.42	2.07	8.29
1st_Peak.T1	PC2	1.51	0.40	0.00	0.78	0.00	0.39	0.28	0.47	1.87
Res.MC	PC3	0.00	6.28	0.00	6.96	4.39	0.00	3.00	4.82	11.91
4th_ML	PC3	4.01	0.00	0.15	4.26	0.00	6.39	1.30	4.06	9.39
4th_Inf.T	PC3	0.45	0.00	0.43	0.00	0.02	0.00	0.08	1.32	1.94
4th_Mid.T	PC3	0.03	0.05	0.00	0.25	0.00	0.19	0.00	0.20	0.38
1st_On.T	PC3	1.82	0.48	0.00	0.78	0.00	0.64	0.00	1.69	2.92
4th_RML	PC3	0.00	0.25	0.00	0.22	0.00	0.09	0.22	0.37	0.57
4th_Peak.T	PC4	4.76	0.00	0.00	5.85	0.00	6.79	2.13	3.22	10.76
1st_RML	n.a	12.00	1.50	2.77	0.00	0.00	0.75	4.11	4.34	13.84
Res.MC_Inf. T	n.a	0.69	0.00	3.74	0.00	0.41	0.00	0.00	5.01	6.85
Res.MC_Mid .T	n.a	0.00	0.00	0.00	0.89	0.00	0.51	1.36	0.94	1.93
1st_Mid.T	n.a	1.07	0.00	0.00	0.33	0.12	0.00	0.26	0.33	1.20
2nd_Inf.T	n.a	0.00	0.00	0.22	0.22	0.00	0.68	0.72	0.41	1.11
2nd_Mid.T	n.a	0.00	0.00	0.10	0.20	0.00	0.00	0.25	0.14	0.37
Res.	n.a	4.73	0.00	1.21	5.33	7.61	0.00	7.82	6.29	15.69
2nd_On.T	n.a	0.00	0.20	0.11	0.08	0.00	0.32	0.08	0.27	0.50
2nd_Peak.T	n.a	0.00	0.17	0.23	0.30	0.00	0.62	0.63	0.30	1.02
3rd_On.T	n.a	0.00	0.35	0.00	0.37	0.00	0.57	0.29	0.81	1.16
4th_On.T	n.a	0.13	0.00	1.26	0.00	0.00	0.00	2.49	4.79	5.56
4th_End.T	n.a	0.00	0.47	0.49	0.00	0.00	0.00	0.00	2.02	2.14
S		0.00	4.43	0.00	12.89	0.00	0.00	9.02	14.82	19.42

* Analytical error derived from the average of analytical errors of *Gross_nested* and *Intra_nested* design; refers to the stage from test sub-sample to test portion and analysis; ¹Variable is captured by both PC1 and PC2; n.a: not applied as loadings of these variables were < 0.60; red values indicate that they exceed the reference limit value (total RSD ≥ 15%)

Table E4-3. Relative contribution (%) of all stages of riffle splitting and shredding from initial sample to test sample (defined as sub-sampling error: SE) and of analytical stage from test sample to test portion (defined as analytical error: AE) to total sub-sampling uncertainty (RSD) for critical TG-DTG points of SRF grouped by principal components (PCs).

Variable number	Variables/ critical TG-DTG points	PCs	Relative contribution to total RSD			Prevalent error to total RSD
			SE (%)	AE (%)	Total (%)	
1	T10%	PC1	86.31	13.69	100.00	SE
2	T20%	PC1	85.84	14.16	100.00	SE
3	T30%	PC1	88.06	11.94	100.00	SE

Variable number	Variables/ critical TG-DTG points	PCs	Relative contribution to total RSD			Prevalent error to total RSD
			SE (%)	AE (%)	Total (%)	
5	T75%	PC1	89.59	10.41	100.00	SE
9	1st_ML	PC1	81.14	18.86	100.00	SE
15	3rd_ML	PC1	79.50	20.50	100.00	SE
16	3rd_Inf.T	PC1	61.52	38.48	100.00	SE
17	3rd_Mid.T	PC1	83.32	16.68	100.00	SE
24	1st_Peak.T	PC1	93.07	6.93	100.00	SE
29	2nd_End.T	PC1	92.61	7.39	100.00	SE
30	3rd_RML	PC1	50.91	49.09	100.00	SE
32	3rd_Peak.T	PC1	55.44	44.56	100.00	SE
33	3rd_End.T	PC1	49.27	50.73	100.00	AE
4	T50%	PC2	88.16	11.84	100.00	SE
10	1st_Inf.T	PC2	89.76	10.24	100.00	SE
12	2nd_ML	PC2	87.68	12.32	100.00	SE
25	1st_End.T	PC2	90.72	9.28	100.00	SE
26	2nd_RML	PC2	93.96	6.04	100.00	SE
24	1st_Peak.T1	PC2	93.07	6.93	100.00	SE
6	Res.MC	PC3	82.32	17.68	100.00	SE
18	4th_ML	PC3	82.40	17.60	100.00	SE
19	4th_Inf.T	PC3	10.52	89.48	100.00	AE
20	4th_Mid.T	PC3	71.07	28.93	100.00	SE
23	1st_On.T	PC3	53.26	46.74	100.00	SE
34	4th_RML	PC3	53.04	46.96	100.00	SE
36	4th_Peak.T	PC4	90.49	9.51	100.00	SE
24	1st_RML	n.a	90.21	9.79	100.00	SE
7	Res.MC_Inf.T	n.a	31.49	68.51	100.00	AE
8	Res.MC_Mid.T	n.a	76.38	23.62	100.00	SE
11	1st_Mid.T	n.a	91.74	8.26	100.00	SE
13	2nd_Inf.T	n.a	86.22	13.78	100.00	SE
14	2nd_Mid.T	n.a	84.72	15.28	100.00	SE
21	Res.	n.a	79.20	20.80	100.00	SE
27	2nd_On.T	n.a	67.36	32.64	100.00	SE
28	2nd_Peak.T	n.a	91.33	8.67	100.00	SE
31	3rd_On.T	n.a	49.73	50.27	100.00	AE
35	4th_On.T	n.a	24.91	75.09	100.00	AE
37	4th_End.T	n.a	10.23	89.77	100.00	AE
38	S		55.77	44.23	100.00	SE

APPENDIX F: Coding of ML algorithm for composition identification of SRF based on its prevalent polymers

Package is given by Rahman (2017):

1. Tools for manipulating datasets in RStudio

```
library(dplyr)
```

```
library(tidyr)
```

```
library(openxlsx)
```

#2. Install packages

```
library(MultivariateRandomForest)
```

```
library(Metrics)
```

#3. MODEL TRAINING

#3.1 Import training datasets

```
DTG_FTIR_SG <- as.matrix(DTG_FTIR_SG) # Input training matrix
```

```
Ymatrix <- as.matrix(Trainign_set) # Output training matrix
```

#3.2 Define tunes for MRF

```
Ntree <- 1000
```

```
Mtry <- 50
```

```
Min_Leaf <- 4
```

#3.3 Run build_forest_predict function

```
Predicted_values_train <-
```

```
build_forest_predict(DTG_FTIR_SG,Ymatrix,Ntree,Mtry,MinLeaf,DTG_FTIR_SG)
```

```
Predicted_values_train <- as.matrix(Predicted_values_train)
```

3.4 Error calculation

3.4.1 Converted the matrix of predicted values into vectors

```
Cellulose_act<-as.vector(Ymatrix[,1])
```

```
Cellulose_pred<-as.vector(Predicted_values_train [,1])
```

```

Hemicellulose_act<-as.vector(Ymatrix[,2])
Hemicellulose_pred<-as.vector(Predicted_values_train[,2])
Lignin_act<-as.vector(Ymatrix[,3])
Lignin_pred<-as.vector(Predicted_values_train[,3])
HDPE_act<-as.vector(Ymatrix[,4])
HDPE_pred<-as.vector(Predicted_values_train[,4])
PP_act<-as.vector(Ymatrix[,5])
PP_pred<-as.vector(Predicted_values_train[,5])
PET_act<-as.vector(Ymatrix[,6])
PET_pred<-as.vector(Predicted_values_train[,6])
PVC_act<-as.vector(Ymatrix[,7])
PVC_pred<-as.vector(Predicted_values_train[,7])

```

3.4.2 Mean Absolute Error (MAE)

```

Cellulose_mae <- mae(Cellulose_act,Cellulose_pred)
Hemicellulose_mae <- mae(Hemicellulose_act,Hemicellulose_pred)
Lignin_mae <- mae(Lignin_act,Lignin_pred)
HDPE_mae <- mae(HDPE_act,HDPE_pred)
PP_mae <- mae(PP_act,PP_pred)
PET_mae <- mae(PET_act,PET_pred)
PVC_mae <- mae(PVC_act,PVC_pred)

mean_absolute_error <- c(Cellulose_mae, Hemicellulose_mae, Lignin_mae, HDPE_mae, PP_mae,
PET_mae, PVC_mae)

```

3.4.3 Root Mean Squared Error (RMSE)

```

Cellulose_rmse <- rmse(Cellulose_act,Cellulose_pred)
Hemicellulose_rmse <- rmse(Hemicellulose_act,Hemicellulose_pred)
Lignin_rmse <- rmse(Lignin_act,Lignin_pred)
HDPE_rmse <- rmse(HDPE_act,HDPE_pred)
PP_rmse <- rmse(PP_act,PP_pred)

```

```
PET_rmse <- rmse(PET_act,PET_pred)

PVC_rmse <- rmse(PVC_act,PVC_pred)

root_mean_squared_error <- c(Cellulose_rmse, Hemicellulose_rmse, Lignin_rmse, HDPE_rmse,
PP_mse, PET_mse, PVC_mse)
```

3.4.4 Root Relative Squared Error (RRSE)

```
Cellulose_rrse <- rrse(Cellulose_act,Cellulose_pred)

Hemicellulose_rrse <- rrse(Hemicellulose_act,Hemicellulose_pred)

Lignin_rrse <- rrse(Lignin_act,Lignin_pred)

HDPE_rrse <- rrse(HDPE_act,HDPE_pred)

PP_rrse <- rrse(PP_act,PP_pred)

PET_rrse <- rrse(PET_act,PET_pred)

PVC_rrse <- rrse(PVC_act,PVC_pred)

root_relative_squared_error <- c(Cellulose_rrse, Hemicellulose_rrse, Lignin_rrse, HDPE_rrse,
PP_rrse, PET_rrse, PVC_rrse)
```

3.4.5 Symmetric Mean Absolute Percentage Error (SMAPE)

```
Cellulose_smape <- smape(Cellulose_act,Cellulose_pred)

Hemicellulose_smape <- smape(Hemicellulose_act,Hemicellulose_pred)

Lignin_smape <- smape(Lignin_act,Lignin_pred)

HDPE_smape <- smape(HDPE_act,HDPE_pred)

PP_smape <- smape(PP_act,PP_pred)

PET_smape <- smape(PET_act,PET_pred)

PVC_smape <- smape(PVC_act,PVC_pred)

symmetric_mean_absolute_percentage_error <- c(Cellulose_smape, Hemicellulose_smape,
Lignin_smape, HDPE_smape, PP_smape, PET_smape, PVC_smape)
```

3.5 Tranfer to excel file

```
Results <-list(PredDTG_FTIR_SG_train, mean_absolute_error, root_mean_squared_error,
root_relative_squared_error, symmetric_mean_absolute_percentage_error, Sum_Squared_Error )

File <-file.choose() #Select an excel file to transfer the results

write.xlsx(Results,file)
```


#4. 10-fold CROSS-VALIDATION

#4.1 Run CrossValidation function

```
CV <- CrossValidation(DTG_FTIR_SG, Ymatrix, 10)
```

#4.2 Transfer matrices for each fold to excel file

```
file1<-file.choose() #Select excel file to transfer 10 fold input training sets
```

```
write.xlsx(CV[[1]],file1)
```

```
file2<-file.choose() #Select excel file to transfer 10 fold input testing sets
```

```
write.xlsx(CV[[2]],file2)
```

```
file3<-file.choose() #Select excel file to transfer 10 fold output training sets
```

```
write.xlsx(CV[[3]],file3)
```

```
file3<-file.choose() #Select excel file to transfer 10 fold output testing sets
```

```
write.xlsx(CV[[4]],file4)
```

#4.3 Run model for the 1st fold of cross-validation

```
trX1 <- as.matrix(Xtrain1)
```

```
tsX1 <- as.matrix(Xtest1)
```

```
trY1 <- as.matrix(Ytrain1)
```

```
tsY1 <- as.matrix(Ytest1)
```

```
F1<- build_forest_predict(trX1,trY1,Ntree,Mtry,MinLeaf,tsX1)
```

```
PredCV1 <- as.matrix(F1)
```

```
fileCV1<-file.choose() #Select excel file to transfer predicted values from 2st fold
```

```
write.xlsx(PredCV1,fileCV1)
```

#4.4 Repeat 4.3 for each fold

#4.5 Repeat 3.3 using the predicted values from cross-validation as test set

#4.5 Repeat 3.4

#5. HOLD-OUT VALIDATION

#5.1 Import hold-out validation datasets

```
Hold_out_DTG_FTIR_SG <- as.matrix(Hold_out_DTG_FTIR_SG) # Input hold-out validation matrix
```

```
Hold_out_Ymatrix <- as.matrix(Hold_out_Ymatirx) # Output hold-out validation matrix
```

#5.2 Repeat 3.3 using the input hold-out validation matrix as test set

#4.5 Repeat 3.4

#6. MODEL TESTING

#Repeat 5 but select the testing matrix instead of hold-out validation matrix