Microwave-assisted processes for biomass valorisation

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Abstract

Lignocellulosic biomass and its major organic components are widely recognised as a renewable resource to produce energy and chemicals. The process imbues the principles of green chemistry and sustainability, therefore, interest in the valorisation of lignocellulosic biomass has significantly increased. Microwave heating has been proven to be an effective, alternative heating method for the pretreatment and conversion of biomass. Herein, different routes for the valorisation of lignocellulosic biomass and its major organic components, such as bamboo, beechwood xylan, and starch, using a microwave as the heating source are reported.

Microwave-assisted pressurised, additive-free, and low-temperature (< 250 °C) pyrolysis was conducted on beechwood xylan using both a constant microwave power and reaction volume, with various degrees of beechwood xylan loading. This allowed for analyses of how and to what extent the reaction pressure and the presence of pyrolysis decomposition products affected the efficiency and product selectivity of the microwave heating process. Due to the different physical states of the volatiles that are released during pyrolysis and that are dependent on the pressure attained, it was demonstrated that xylan loading had a significant effect on the distribution of the final products.

Microwave-assisted organosolv experiments were performed on bamboo powders using a fractionation approach. The effects of reaction temperature, solvent composition, and catalyst loading on the organosolv process were evaluated by statistical methods, to determine the effects of operating variables and optimizing the process towards a selective fractionation. Moreover, the direct application of organosolv lignin as an additive for sunscreen was briefly tested.

A novel mesoporous material, Starbon®, was produced from starch by an expansion, retrogradation, and carbonisation approach. By introducing microwave-assisted heating to the starch expansion process, the total production time was significantly reduced, resulting in a more energy-efficient process.

List of Contents

List of Figures

List of Tables

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Author's declaration

I declare that this thesis is a presentation of original work and I am the sole author. This work has not previously been presented for an award at this, or any other, University. All sources are acknowledged as References. Some of the results presented herein were obtained by, or in collaboration with other co-workers. They are fully acknowledged in the list below along with their corresponding institution.

Tianzong Li

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Piece of work	**Collaborator/institution**
Elemental analysis (CHN)	Chemistry Department service, University of York
ICP-MS analysis	Chemistry Department service, University of York
Total organic carbon analysis	Dr. Javier Remon Nunez, Department of Chemistry, University of York
HPLC analysis	Dr. Hannah Brier, Department of Chemistry, University of York
GPC analysis	Dr. Javier Remon Nunez, Department of Chemistry, University of York
SEM microscopy	Dr. Meg Stark, Department of Biology, University of York
Dielectric loss factor measurement	Engineering faculty, University of Nottingham

Chapter 1 Introduction

1.1 PROJECT AIM.

This project aims to study capability of microwave heating in valorisation of biomass and its major components. As a more controllable heating method, microwave heating is used throughout the project.

Chapter 1 presents a general review of "Green Chemistry" and biorefinery as well as the application of microwave heating technology in biorefinery.

Chapter 2 describes the microwave-assisted additive-free pressurised pyrolysis of hemicellulose for the generation of bio-oil and bio-char. In this chapter, a fast (<10 min) and low temperature (< 250 °C) closed vessel doping-free microwave assisted pyrolysis of xylan was investigated. It has demonstrated that by changing the initial sample mass, the final product composition could be changed significantly. It can be applied for selectively production of bio-oil or bio-char.

Chapter 3 addresses a novel microwave-assisted organosolv system for bamboo selective fractionation. The influence of temperature, solvent ratio and catalyst loading were investigated in detail to achieve an optimal fractionation effect.

Chapter 4 briefly describes the application of microwave-assisted starch expansion for a bio-renewable mesoporous material Starbon® production and reports the detailed production method.

Chapter 5 describes conclusions (including future work) of the PhD project.

1.2 PREAMBLE: SUSTAINABILITY, A SOLUTION TO CURRENT CHALLENGES.

With rapid technology development and economic growth in the past 100 years, we are consuming more energy and materials than ever before. The fact that we live on a planet with limited resources and limited capacity to absorb waste should not be ignored [1]. Clark et al. introduced an equation to express the relationship among Earth's Capacity (EC), world's population (P), the economic activity of an individual (C), and a conversion factor between activity and environmental burden (B) [2]. The equation is expressed as follows [2]:

$$EC=P\times C\times B$$

Since we live on a single planet, EC is a constant number in this equation. Both the global population (P) and economic activity of an individual (C) continue to increase. In order to achieve sustainability, the conversion factor between activity and environmental burden (B) must be reduced. Two ways have been proposed to reduce B:

1) Dematerialisation: use fewer resources and produce less waste.
2) Transmaterialisation: use different materials and treat "waste" as resources.

Compared to dematerialisation, transmaterialisation is easier to be accepted since it does not require individuals to reluctantly lower their living standard or change their desired life style.

Finding renewable resources to generate the chemicals, energy as well as materials for growing population (P) and increasing individual expectations (C) needs can significantly reduce the environmental burden (B). Due to their abundancy and abundant availability, lignocellulosic materials such as forest products (hardwood

and softwood), agricultural residues (e.g. wheat straw, corn stover, sugarcanes), and dedicated crops (salix, switchgrass), are suitable candidates for renewable resources. In most lignocellulosic materials, nearly 90% (by weight) of the dry matter is stored in the form of cellulose, hemicellulose, lignin, and pectin, whereas waxes and inorganics are the main components in the remainder 10% of weight [3]. Plants have evolved a complex interconnected polymer cellulose, hemicellulose and lignin structure that can cause recalcitrance against micro-organisms enzyme decomposition and hydrolysis in nature [4]. Therefore, to fully utilise lignocellulosic materials, proper pre-treatment is necessary. The pre-treatment can be broadly classified into thermal conversion and bio-conversion. In some cases, both thermochemical conversion and biochemical conversion are used simultaneously to achieve an optimal effect [5].

1.3 GREEN CHEMISTRY

Chemistry is a branch of science that focuses on transformations and the use of these transformations to form new substances. Development in the field of chemistry dramatically changed our living standard and lifestyle. According to the European Chemical Industry Council (CEFIC) report, in 2015, the world's total chemical industry generated a total revenue of €3,534 billion, which almost doubled the total sales in 2001, and grew by 14.0 percent from €3,100 billion in 2014 [6]. Considering Asian countries, especially China's rapid economic growth, it is reasonable to foresee that the total turnover of the chemical industry will continue to show a growing trend in the next few years. When averaging the €3,534 billion in sales among everyone on this planet, a single person would have consumed about €500 in chemical products in the year 2015 alone.

Also in the European Union (EU), growth of the chemical industry is dramatic; the total revenue increased by nearly 60% in the past 20 years [6]. The chemical industry has always been an important industry sector in the world and a total of 4.8 million people are employed by chemical companies or work in the chemical sector through indirect employment. However, behind this flourishing industry, problems still exist. Among all these problems, sustainable raw material and waste treatment are the two most important issues that should not be neglected because they may negatively affect the health of human beings and the sustainability of our planet.

In the past, raw materials for the chemical industry were mainly derived from natural mineral resources such as coal, crude oil, natural gases, and metals. The production process of these resources takes millions of years; therefore, the total stock of natural resources is limited. Several natural resources cannot even be reproduced by nature. With the rapidly growing global economy, the chemical industry requires more and more natural resources to fulfil its needs. The increasing demand of natural resources always causes tension among nations, which often results into war, starvation, and several other anti-humanity crises. Thus, sourcing and utilising renewable raw materials are considered effective ways to solve these problems.

Apart from raw material sustainability, global waste is another major issue that continues to be a challenge. In the chemical industry, it is common that side products are produced along with the desired products. However, in certain chemical industry sectors, the number of side products outweigh the desired products. When by-products cannot be utilised properly, they will become chemical waste. Moreover, the desired products will also become chemical waste after

termination of their life cycle. Given that all the waste in the world is made up of chemicals in some fashion, the basis of distinguishing environmental hazard waste from environmental benign waste is whether the waste or its additional chemical reaction products are generated under storage conditions, will get into air, water, soil, and organisms, where it can result in undesired or unforeseen effects to the environment. In the 1860s, chemists and the government first started to notice the negative effects of the chemical production process on the environment. In 1863, the British Alkali Act was introduced because the manufacturing of sodium carbonate by the Leblanc process (Figure 1) caused significant air pollution and economic loss [7].

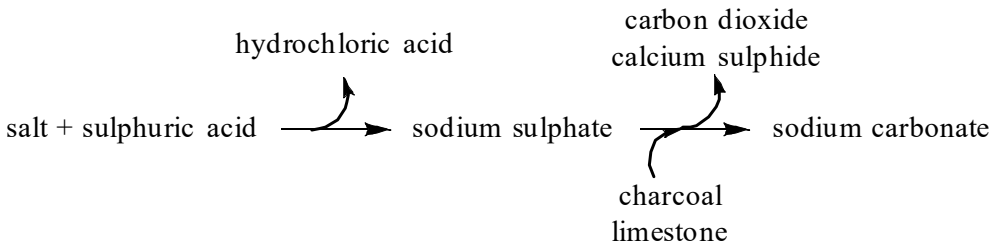


Figure 1: Leblanc process for sodium carbonate production.

In 1987, the Montreal Protocol was introduced as the first worldwide environmental legislation designed to protect the ozone layer by phasing out several ozone-depleting substances [8]. Since the Montreal Protocol was issued, the ozone hole has slowly been recovered [9]. Recovery of the ozone layer in Antarctica has proven that strict regulation is effective in protecting the environment [10].

However, not all pollution-associated issues have attracted as much attention as the ozone layer depletion; these additional issues could also significantly affect a

human being's sustainability. Issuing regulation is only a temporary solution. The costs that are associated with issuing a new regulation can be enormous and it is just not possible to issue a regulation for every single environmental problem. In the early 1990s, influenced by the Pollution Prevention Act of 1990, several scientists started to think differently and introduced a philosophy that addressed the problems from the "cause". They proposed the question of why we must rely on hazardous substances in so many industrial processes [11, 12]. These scientists hypothesized about the impact of the chemists' inventions on the planet and suggested that perhaps the hazardous substances were simply used because no one had ever tried to use a different approach. This novel philosophy is known as "green chemistry".

The concept of "green chemistry" was first introduced by John Warner along with Paul Anastas. In 1998, Warner and Anastas jointly published a book, entitled: Green Chemistry: Theory and Practices. In this book, the concept of "Green Chemistry" was formally introduced with a "how-to guide at the molecular level", i.e. the "12 guiding principles of green chemistry" (see Appendix A) [13].

The "12 principles" focus on three key aspects: 1) use less hazardous reaction substances; 2) optimize the reaction process; 3) waste and pollution control. At first glance, these principles may seem common sense, by further understanding the twelve principles, it can be appreciated that these principles not only consider reducing the environmental impact but also consider the sake of the chemists involved. For example, using "safer solvents and auxiliaries", is not only better for the public and environment, but also considers the risk of chemists. Chemists are usually the individuals who work closely with solvents and chemicals, and are at high risk of exposure. Another example is "design for energy efficiency", which

focuses on saving energy, however it also saves the hassle for the experimenters [5].

The chemistry branch generally focuses on the transformation of substances from starting materials to form a new product [14]. The beauty of chemistry is that this transformation can be delivered in multiple ways. In the past, the environmental impact of the chemical industry and a human beings' sustainability was not a major concern. Interest was more focused on how to generate the compounds that were required. Consequently, a significant amount of non-renewable resources were used, in which hazardous solvents, auxiliaries, high temperature, and elevated pressure were employed during the production process. "Twelve principles of green chemistry" provides chemists with a guide of reconsideration and evaluates the old hazardous production strategy. "Twelve principles of green chemistry" also conveys chemists that they are smart enough to design novel and better methods for the production of their desired products (benign by design). This is what the "Twelve principles of green chemistry" tells us.

After introduction of the concept of "Green Chemistry", big corporations such as Monsanto, Dow, Merck, Pfizer, and DuPont along with many start-up companies accepted the concept [15]. As a result, many technologies are currently used in real production, including safer latex paints, safer household cleaning products, Saran Wrap to textiles made from starch, selective pesticides, greener dry-cleaning agents, critical carbon dioxide caffeine extraction, drugs such as Advil, Zoloft, and Lipitor products [16-20].

1.4 THE BIOREFINERY CONCEPT

1.4.1 Definition

The biorefinery is a facility, or a network of facilities, that transforms biomass into energy, biomaterials, and chemicals [1]. By using [21]this approach, the value of biomass can be maximised, while the production of waste can be minimised . Due to limited resources and capacity of waste on our planet, the biorefinery concept gained increasing attention in both industry and academia [22, 23]. Per product category, biorefinery is very similar to petrol-refinery in which energy and chemicals are produced from fossil resources, whereas in biorefinery energy and chemicals are produced from biomass (see Appendix B).

Considering the wide availability, low price, high volume, and high sustainability properties of biomass, biorefinery has a huge potential to substitute the non-renewable and high-cost traditional petrol-refinery. In fact, biorefinery has already partially substituted the petrol-refinery in areas such as fuels (e.g. bio-ethanol, bio-diesel) [24], several commodity chemicals (e.g. vinyl acetate, acetic acid) [25], and materials (e.g. starch-based plastic) [26].

Although the biorefinery is not yet capable to fully substitute the petrol-refinery, over time, the biorefinery technology will become more and more sophisticated and outgrow petrol-refinery. The Joint European Biorefinery Vision for 2030 pointed out that by 2030 a significant proportion of the overall European demand for chemicals, energy and materials will be coming from biomass as a feedstock [27]. Clark et al. summarised the Joint European Biorefinery Vision for 2030 into three major targets regarding biorefinery products [1]:

- Bio-based chemical products are expected to take up 30% of the overall chemical production. For some high added value products, the proportion may even be greater than 50%.

- Biofuels will supply 25% of Europe's transportation energy, with advanced fuels (in particular, bio-based jet fuels) taking an increasing share.
- Biomass will provide at least 30% of Europe's heat and power generation.

1.4.2 Different types of biorefinery:

According to the literature, the biorefinery has been classified into three categories [28, 29]:

Table 1: Phases of biorefinery.

Biorefinery type	Feedstock	Process	Products	Example
Phase I	Single	Single	Single	Biodiesel process in Europe [30]
Phase II	Single	Multiple	Multiple	Novamont plant in Italy [1]
Phase III	Multiple	Multiple	Multiple	No commercial example exist, however this is the most advanced type of biorefinery and extensive work is being performed [1].

1.4.2.1 Phase I biorefinery

As shown in Table 1 and Figure 2, Phase I biorefinery only uses one feedstock and a single process to produce one major product. Phase I biorefinery has nearly no flexibility to recover investment and operating costs [2].

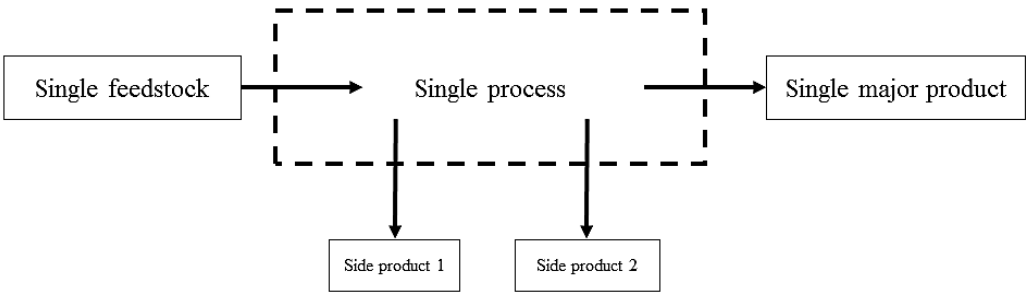


Figure 2: Schematic showing Phase I biorefinery. (Modified from Espinoza et al. [31]).

In Phase I biorefinery, several side products may be produced, however these side products are not biorefinery products. For example, in Europe, oil crop such as rape seeds are widely used as a feedstock for the production of biodiesel [30]. During the process, rape seeds can also be prepared into meals and glycerine for other purposes. However, the major biorefinery product is biodiesel, therefore, the process is still considered Phase I biorefinery.

1.4.2.2 Phase II biorefinery

Like Phase I biorefinery, Phase II biorefinery (Figure 3) can only process with one feedstock. The main difference between Phase I and Phase II biorefinery is that Phase II biorefinery produces different types of end-products, such as energy, materials, and chemicals and can therefore respond to market demand in a more flexible way.

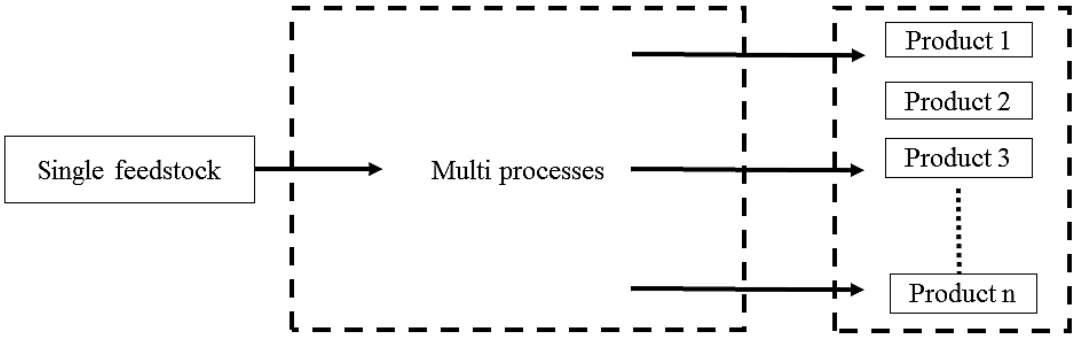


Figure 3: Schematic showing the Phase II biorefinery process. (Modified from Fernado et al. [29]).

Ultimately, in almost all cases, Phase I biorefinery can be upgraded to Phase II biorefinery. If in the previous rape seed biodiesel production example, side products were identified and directly converted into energy, chemicals or biofuels, the system will be upgraded to a Phase II biorefinery process.

1.4.2.3 Phase III biorefinery

Phase III biorefinery, as shown in Figure 4, is the most advanced type of biorefinery. Similar to Phase II biorefinery, in Phase III biorefinery a variety of products can be produced, such as energy, chemicals and materials. Moreover, Phase III biorefinery can also use various types of feedstock and processing technologies to produce multi-types of industrial products to feed the need of modern society [1]. The flexible biorefinery type can provide a wide range of bio-products to meet the market demands, and maximise the return on investment (ROI) [27]. In addition, due to the multi-feedstock feature of Phase III biorefinery, a selection of the most profitable feedstock combinations is possible for highly integrated biorefineries [32]. Unfortunately, no commercial Phase III biorefinery exists, however, research into Phase III biorefinery is extensively carried out around the world.

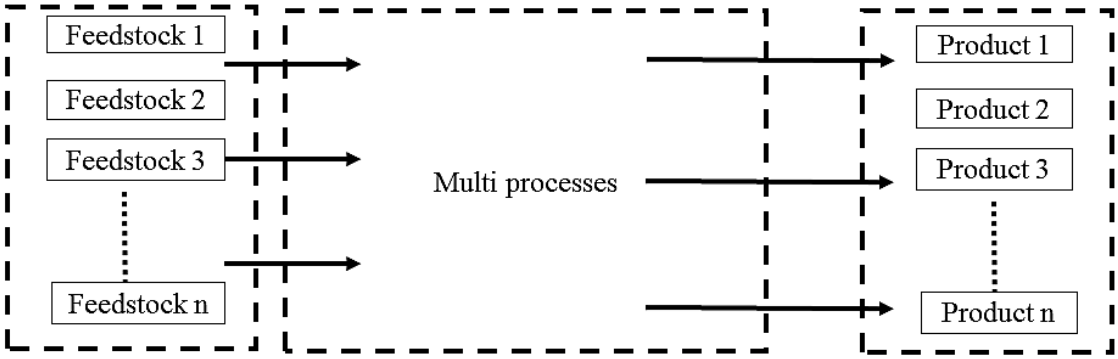


Figure 4: Schematic showing Phase III biorefinery (modiefied from Kamm et al. [33]).

1.5 LIGNOCELLULOSIC BIOMASS AS A FEEDSTOCK

For the scope of this thesis, bamboo, xylan and starch were all considered feedstocks, therefore this section gives a brief overview on the chemistry of lignocellulosic biomass, comprising cellulose, hemicellulose, lignin, and starch-based biomass.

Lignocellulosic biomass refers to plant biomass that is composed of cellulose, hemicellulose and lignin. The weight percentage of each component varies from species to species, however in general, typical woody biomass contains 35-50% cellulose, 25-30% hemicellulose and 15-30% of lignin, as well as 5-10% organic extractives and inorganic minerals [34-36]. Figure 5 shows the general constituents of lignocellulosic biomass, and Table 2 lists the cellulose, hemicellulose and lignin content of several selected common plant resources. In the biorefinery industry, lignocellulosic biomass is an ideal feedstock for the production of chemicals, energy and materials. Compared to the traditional fossil resources, lignocellulosic biomass has many advantages, including a wide geographical distribution, relatively low costs, easy access, and high volume [37-39]. Globally, around 1.8×10^{11} tonnes of lignocellulosic biomass are produced annually, which is more than 90% of total biomass production. Among these, about $0.08\text{-}0.2 \times 10^{11}$ tonnes ends up as waste, which is a massive an potential feedstock for biorefineries [40, 41].

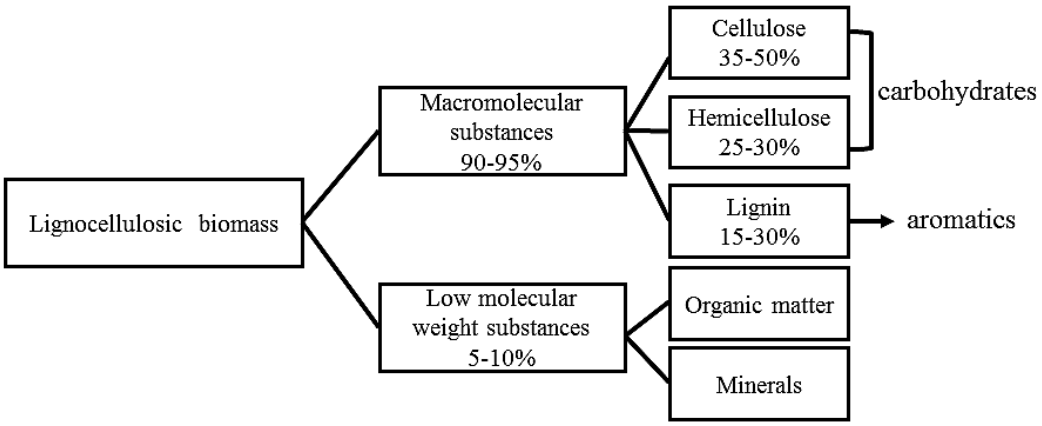


Figure 5: General composition of lignocellulosic biomass (wood and other plant biomass) [34-36].

Table 2: Typical cellulose, hemicellulose and lignin contents of selected common plant resources [41-45].

Plant	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Wood	35-50	25-30	15-30
Wheat straw	33-40	20-25	15-20
Switch grass	30-50	10-40	5-20
Sugarcane bagasse	19-24	32-48	23-32
Corn stover	37	21	13-21
Rice straw	32	24	18
Bamboo	45	26	21

1.5.1 Cellulose

Cellulose is a fibrous, tough, water-insoluble substance, which can be found in the protective cell walls of plants, particularly in stalks, stems, trunks and all woody portions of plant tissues [46]. In the cellulose linear structure, glucose units are linked by β-(1,4) -glycosidic bonds [47]. Typically, the average molecular weight

of cellulose is around 100,000 Da [48]. Cellulose contains extensive inter- and intra- molecular hydrogen bonds; these hydrogen bonds tightly connect the glucose units and promote the cellulose crystalline structure. The chemical structure of cellulose is illustrated in Figure 6.

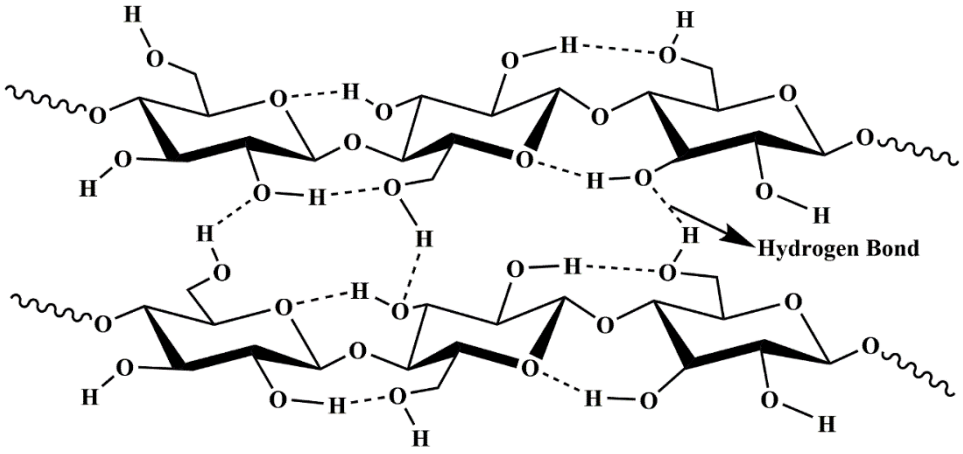


Figure 6: Fragment of a cellulose chain with hydrogen bonds [47].

1.5.2 Hemicellulose

Hemicelluloses are low-molecular weight polysaccharides, which, in plant cell walls, are associated with cellulose and lignin [49]. Unlike cellulose, which structure only contains glucose units, hemicellulose consists of a diverse group of heterogeneous polysaccharides [49]. Among them, pentoses (C5 sugars) such as xylose, arabinose, and hexoses (C6 sugars) such as mannose, glucose and galactose as well as some uronic acids, such as glucuronic acid are the major constituent monosaccharides in hemicellulose. The major constituent monosaccharides are illustrated in Figure 7.

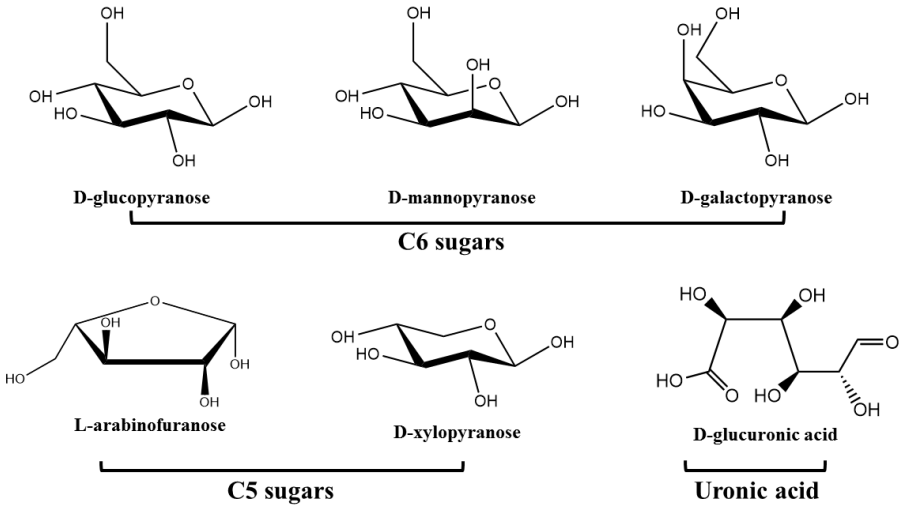


Figure 7: Major constituent monosaccharides of hemicellulose.

In hemicellulose, the major constituents are linked by β-(1,4)-linkage with an equatorial configuration at C1 and C4, with a degree of polymerisation (DP) ranges from 500 - 3,000, which is much lower than that of cellulose (DP ranges from 7,000 – 15.000) [50, 51].

There are many different types of hemicellulose that can be found in plant cell wall. The classification of hemicellulose types depends on hemicelluloses' backbone molecule structure. In general, hemicellulose can be classified four major categories [52]:

1. xyloglucans (xylans)
2. mannoglycans (mannans)
3. xylo-glucans
4. β-Glucans

1.5.2.1 Xylan

Xylan is the most dominant type of hemicellulose in most plants cell wall. Xylan is also the second most abundant polymer in nature, and roughly accounts for over 30% of the total renewable biomass that is available on our planet [53]. Xylan is a collective name of hemicellulose that contains xylose as its dominant backbone units [52]. Xylan can be sub-grouped into (i) homoxylans: linear polysaccharides commonly found in seaweeds; (ii) glucuronoxylans: most common type of xylan that can be accessed in dicotyledon plants woody tissue; (iii) (arabino)glucuronoxylans: normally exist in tropical softwoods; (iv) arabinoxylans: typical hemicellulose components in flour (starchy endosperm) and bran (outer layers of cereal grains), also exist in seeds of other monocotyls plants such as bamboo shoots and rye grass (v) (glucurono)arabinoxylans: dominant type of hemicellulose in lignified tissues of grasses and cereals, such as straw, stems, stalks (vi) heteroxylans: contain a backbone molecule that is similar as homoxylans, however, the side chains are heavily substituted by a variety of oligosaccharides, causing it to be a highly viscous substance [54]. Different types of xylan are bio-synthesised from various plants, therefore, the backbone molecules present

different components and properties. The types of xylan mentioned above show structural differences and variation in side chain types. A typical xylan structure is shown in Figure 8.

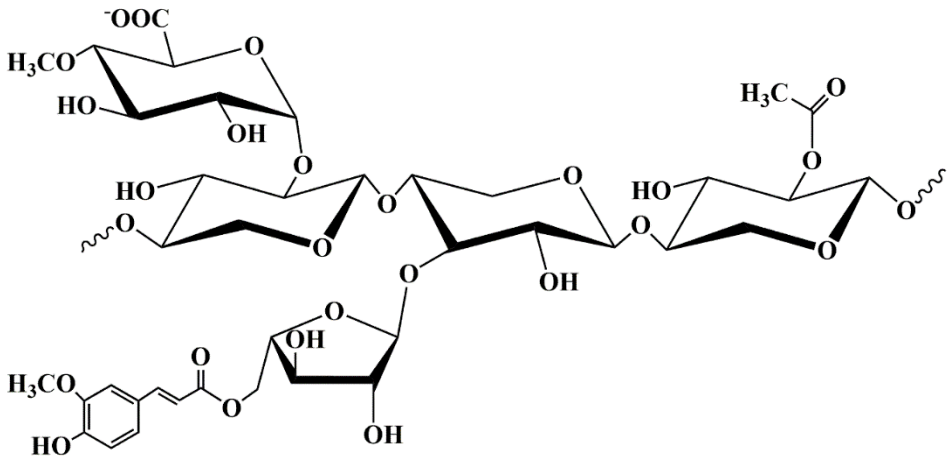


Figure 8: Typical structure of xylan [55].

1.5.2.2 Mannans

Mannans are usually classified into galactomannans and glucomannans, or as a combination of glacto-glucomannans. A typical glacto-mannan structure is presented in Figure 9. Both galactomannans and glucomannans are made up of β-(1-4)-linked manno-pyranose units. The differences between galactomannans and glucomannas are due to the differences in galactose content of the backbone molecule.

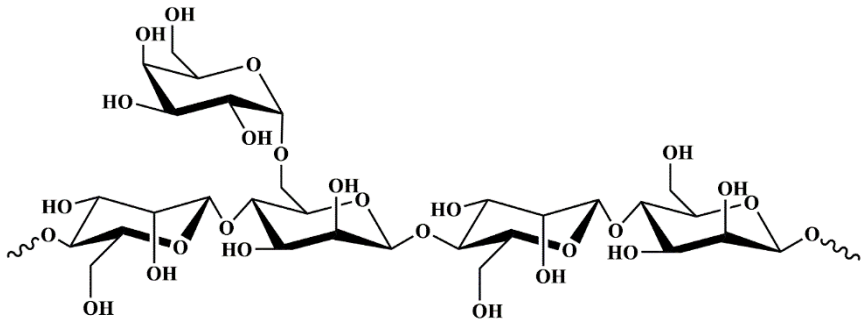


Figure 9: Primary structure of galacto-mannan [52].

1.5.2.3 Xyloglucan

Xyloglucan is a type of hemicellulose that mainly consists of a β-(1-4)-linked glucanpranan backbone with xylo-pyranose residue substitution. It can be regarded as the low degree of polymerisation (DP) cellulose with the substitution of xylose in the side chain. In the cell wall of plants, xyloglucan mainly serves as the building material of the cell wall of higher plants. The primary structure of xyloglucan is shown in Figure 10.

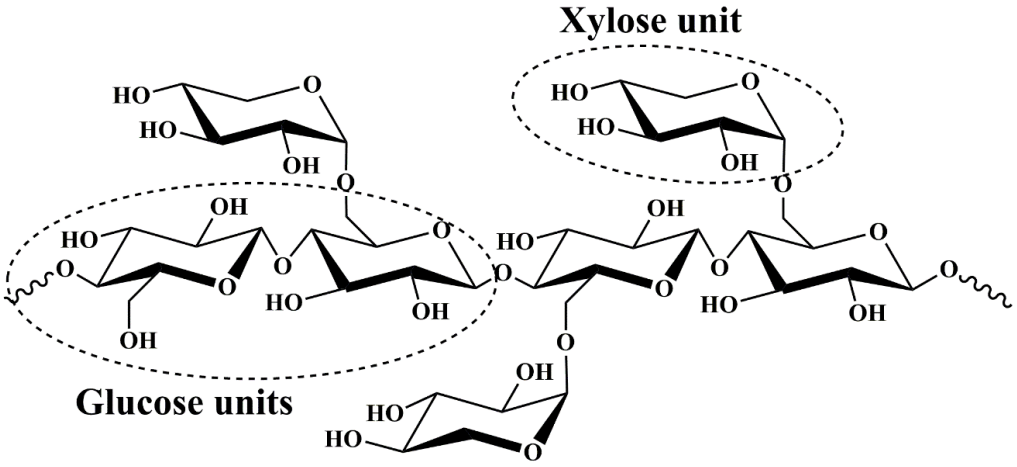


Figure 10: Primary structure of xyloglucan [52].

1.5.2.4 β-glucan

β-glucan is a type of hemicellulose that exclusively consists of β-(1-4)-linked glucose units. β-glucan is biosynthesised alongside cellulose, however, in β-glucan, the DP is significantly lower. A typical β-glucan structure is illustrated in Figure 11) [56].

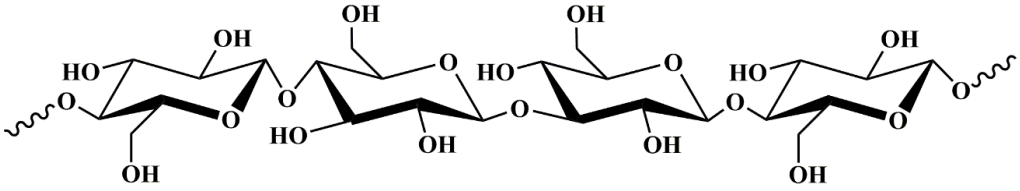
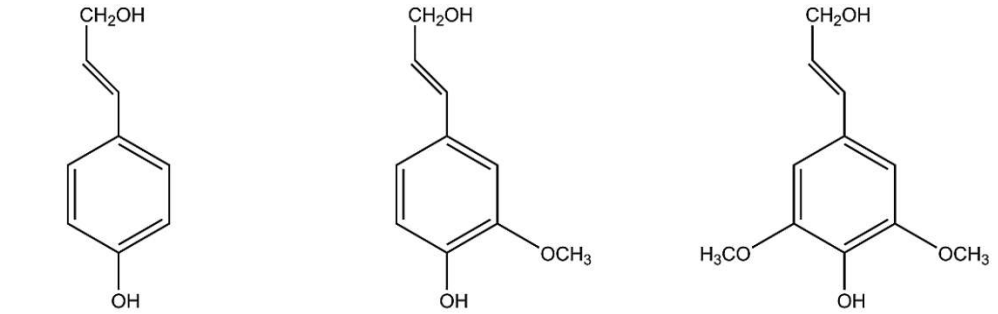


Figure 11: Primary structure of β-glucan [52].

1.5.3 Lignin

Lignin is the most dominant aromatic natural polymer in the world, and approximately 15% to 40% of the dry weight of terrestrial plants are contributed by lignin [57]. Lignin is the third major component of lignocellulosic biomass, and is one of the most underutilised fractions of lignocellulosic biomass [58]. In the cell wall, lignin surrounds the outer layers of polysaccharide fibres, and thereby protects cellulosic fibres from microbial, fungal and chemical corruption. Moreover, lignin also provides structural integrity and rigidity to the cell wall [59-61].

Structurally, lignin is a complex aromatic cross-linked heteropolymer that is mainly derived from three hydroxycinnamyl alcohol monomers (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) that differ in their degree of methoxylation [62]. The structure of the three major building blocks is shown in Figure 12, and a fragment of the structure of natural lignin is shown in Figure 13. When incorporated into the lignin polymer, these three monolignols produce p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) phenylpropanoid units, respectively.



***p*-coumaryl alcohol** **coniferyl alcohol** **sinapyl alcohol**

Figure 12: Chemical structure of lignin building blocks.

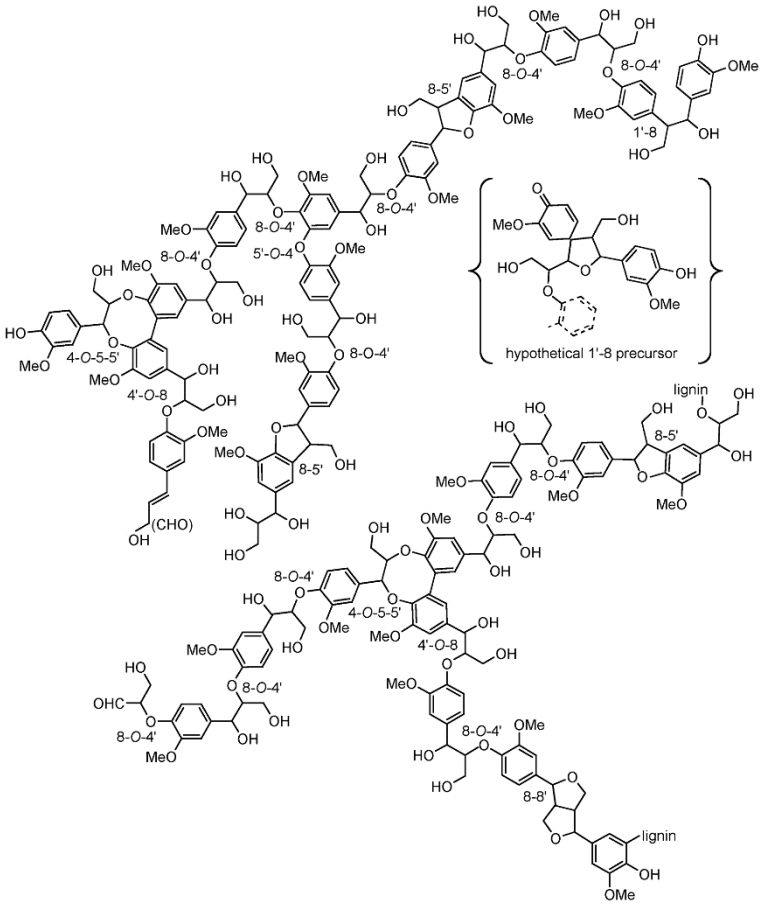


Figure 13: Representative fragment of the lignin structure (adapted from [63]).

1.5.4 Starch

Starch, which accumulates in plants storage organs such as tubers or seeds in a granular form, is the most important energy reserve in higher plants [64]. The annual global production of starch is around 2.5 billion tonnes [65]. The European starch industry is increasing and from 2004 to 2015, the starch production increased by 23%. Currently, the EU produces about 10.7 million tonnes of starch from EU wheat, maize and potatoes each year [66]. Among these, around 9.3 million tonnes of starch is utilized for both food and non-food applications. A total of 61% of starch is used in food applications such as confectionery and drinks, whereas 38% of starch is used in corrugating, paper, and in pharmaceutical and chemical industries. The proportion of each starch application is shown in Figure 14.

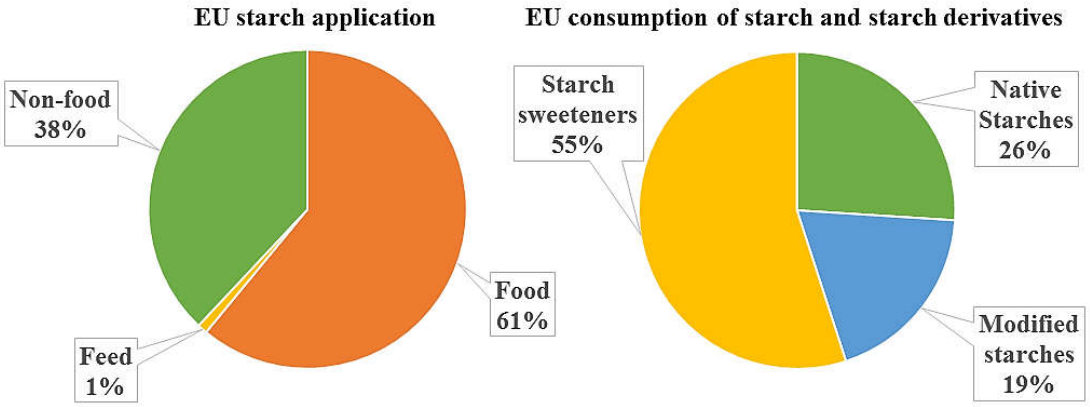


Figure 14: Starch industry market facts [66].

Considering that in Europe 10.7 million tonnes of starch is produced each year, and only 87% is utilized, it can be estimated that a large amount of starch is currently being underutilised or wasted. Therefore, it is of utmost importance to explore valorisation routes for underutilised starch to increase usage and reduce waste [67]. The chemical composition of starch largely depends on the botanical origins. The origin of starch also affects the physical properties of starch, such as form, shape and functionality [68]. Starch is composed of amylose and amylopectin. These two types of α-glucans take up about 98 – 99% of the dry weight of starch [68]. Moreover, a small trace of lipids, free fatty acids, proteins, and inorganic minerals can also be found in starch granules [68]. The ratio of amylose and amylopectin in starch can significantly affect major properties, including gelatinisation temperature, gelling rate, viscosity, and mechanical strength of the starch polymer [69].

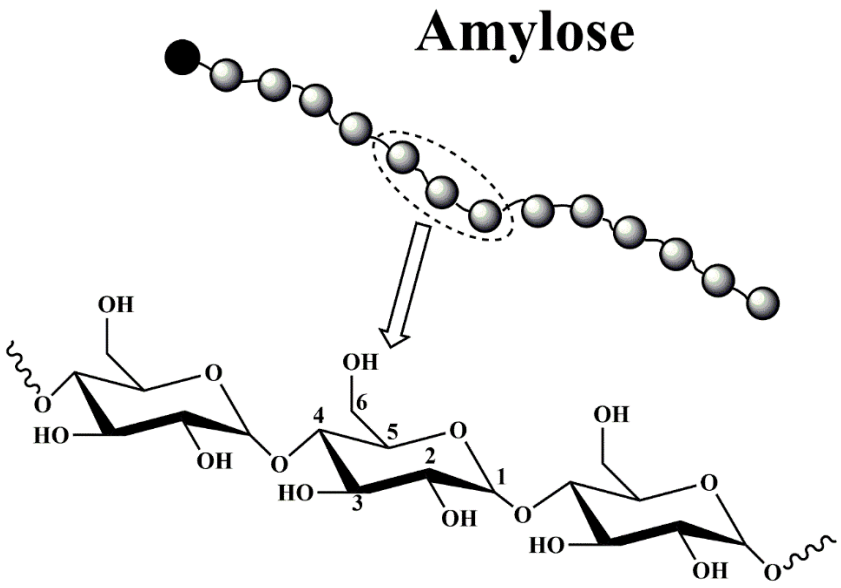


Figure 15: Chemical structure of amylose [68, 70].

Amylose is a linear polymer made up of approximately 99% of unbranched (1-4)-linked α-glucans. In contrast, amylopectin has a highly-branched structure, consisting of a (1-4)-linked α-glucose backbone, with (1-6)-linked α-glucose in the branching links (Figures 15 and 16) [68, 70]. The DP of natural starch ranges from 1,000 - 10,000 glucose units, with an average molecular weight between 10^5 - 10^6 Da [68, 70].

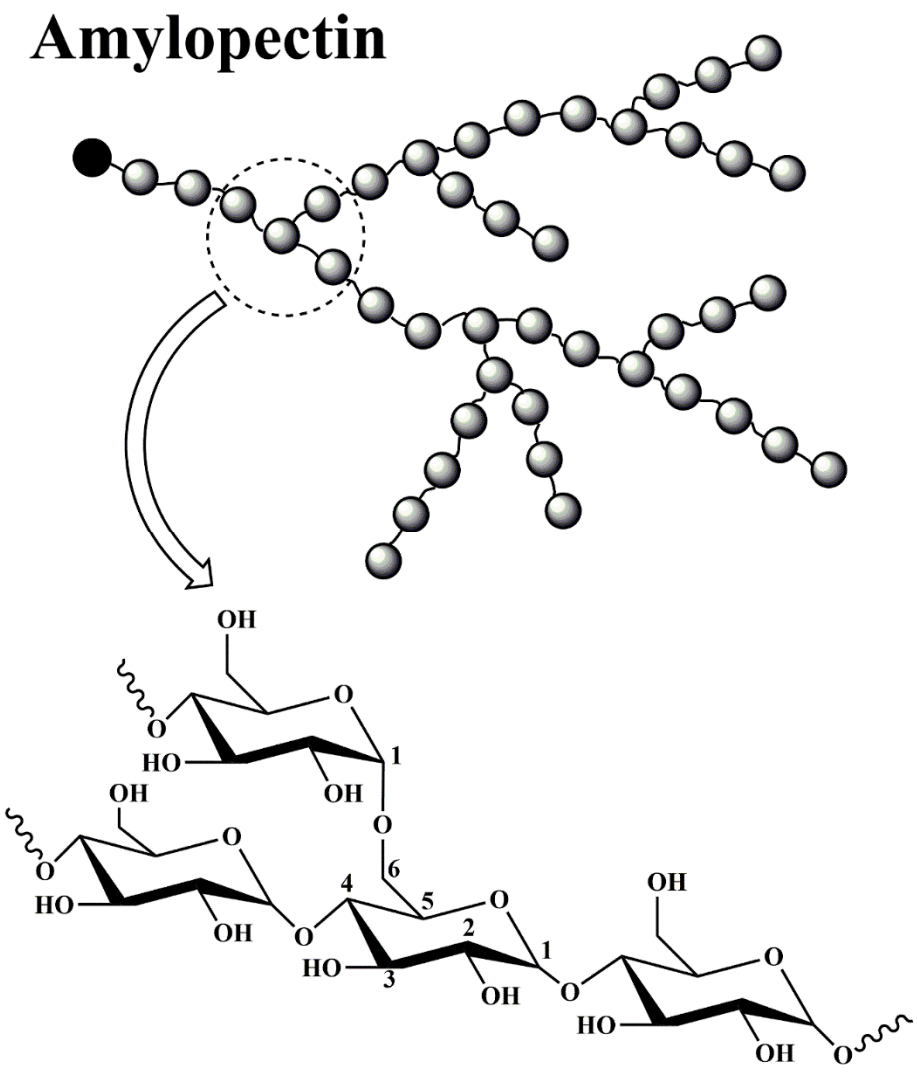


Figure 16: Chemical structure of amylopectin [68, 70].

1.6 BIOREFINERY PROCESSING METHODS

In order to maximise the utilisation of lignocellulosic biomass, different treatment methods have been proposed. Through different conversion methods, products such as fuels, chemicals, or forms of energy have been generated from lignocellulosic biomass. In general, conversion pathways can be classified into two major types, i.e. thermo-chemical conversion and bioconversion (Figure 17).

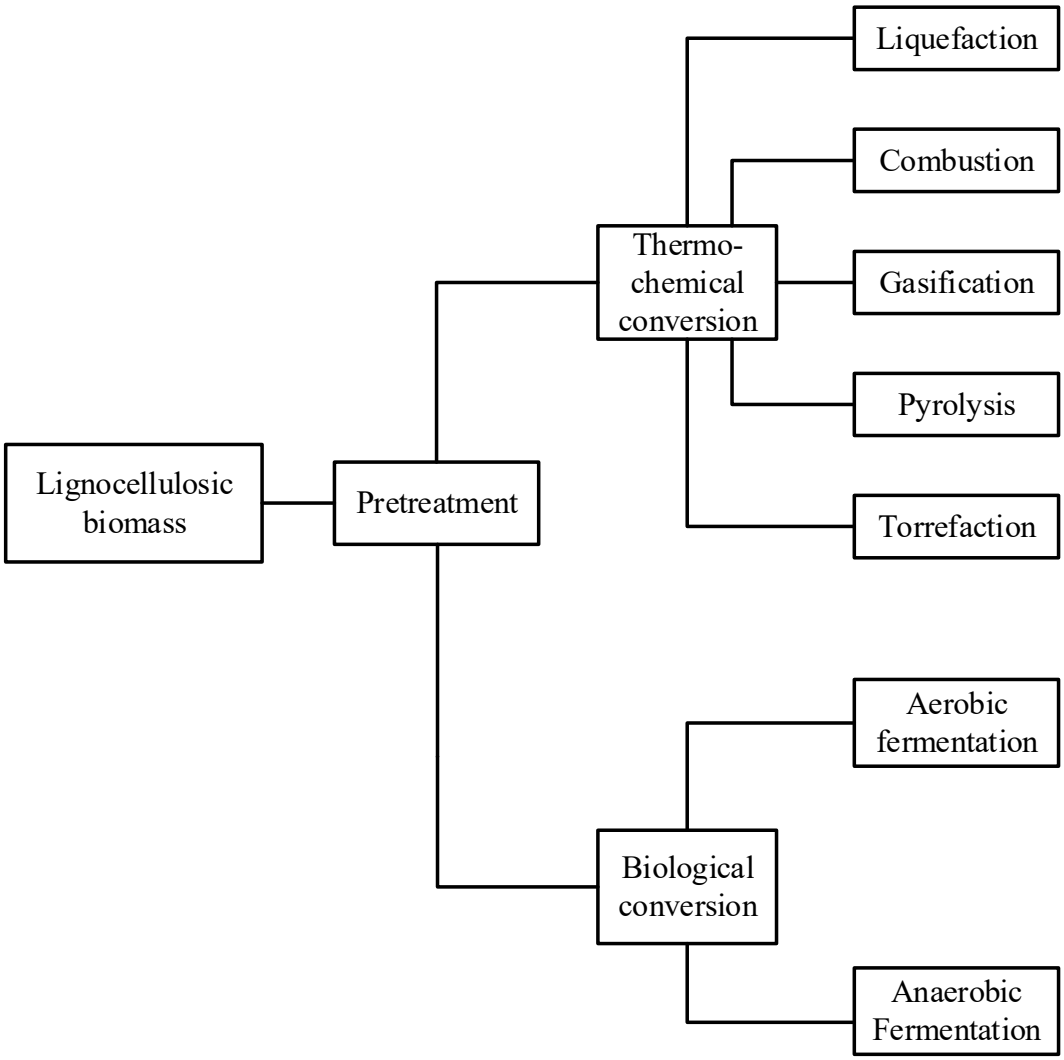


Figure 17: Flowchart describing the two primary types of biomass conversion methods.

The thermo-chemical conversion methods involve thermo-decomposition of biomass into products. Liquefaction, combustion, gasification, pyrolysis, and torrefaction, as well as hydrothermal biomass activation, are the major techniques used for thermo-chemical conversion. In biological conversion processes, lignocellulosic biomasses are converted to fermentable components, which will then be converted into various products with the help of microbes such as bacteria and fungi.

In a previous study, it was found that neither thermo-chemical conversion nor biological conversion could efficiently convert biomass into products [71]. The main reason for this was that in most cases, cellulose, hemicellulose, and lignin are tightly bonded together, and this firm structure prevented the biomass from being decomposed easily [71, 72]. Therefore, a pretreatment process is required for the majority of biomass conversion processes. By using a proper pretreatment approach, the efficiency of biomass conversion can be significantly improved. Moreover, pretreatment methods can potentially help to alter lignocellulosic biomass crystallinity and change the structure and chemical composition, thereby increasing the possibilities of the biorefinery products.

1.6.1 Pretreatment

The purpose of a pretreatment method is to increase the efficiency of the biomass conversion process and to eliminate undesired biomass fractions. Ideally, the pretreatment process should be carried out in an efficient and environmentally friendly manner. In order to realise this, several different technologies are used in the biomass conversion pretreatment stage [73].

In general, pretreatment processes can be classified into four major categories, including mechanical pretreatment, physical pretreatment, chemical pretreatment, and biological pretreatment (Table 3). Pretreatment is a critical step to maximise the efficiency of biomass conversion. Each pretreatment method has its advantages and disadvantages, in practical research, the selection of pretreatment method depends on the biomass type and the working environment. There is no omnipotent pretreatment method.

Table 3: Comparison of different pretreatment methods.

Major Categories	Sub Categories	Brief Explanation
Mechanical Pretreatment	Chipping, Grinding and Milling	Reduction of size and crystallinity of lignocellulosic materials.
	Densification	Densify the biomass to reduce transportation and handling costs [74].
Physical Pretreatment	$ScCO_2$ and Natural Solvent Extraction	Using the solvating properties of supercritical CO_2 or natural solvent for the extraction process [75].
	Ammonia Fibre Explosion	A combination of physical and chemical digestion pre-treatment approach for a more effective biological conversion [76].
	Supercritical Water Treatment	Environmental benign solvent, with a low dielectric constant and a reduced number and persistence of hydrogen bonds, which provides a single fluid reaction condition [71].
Chemical Pretreatment	Acid Hydrolysis	To hydrolyze hemicellulose, break lignin seal and decrease the crystallinity of cellulose for further enzymatic hydrolysis [77].
	Alkaline Hydrolysis	Delignification and removal of part of hemicellulose [78].
	Ozonolysis	Use ozone to degrade lignin and a part of hemicellulose [79, 80].
Biological Pretreatment	Fungal Digestion	Lignin removal [71, 81].

1.6.2 Conversion methods

After completion of the pretreatment stage, the biomass should be relatively pure and easier to handle. Through different conversion technologies, the biomass can be transformed into different types of desired chemicals, materials, fuels, or energies [36]. There are two major types of conversion methods: thermo-chemical conversion and bioconversion (Figure 17). Thermochemical conversion involves thermal decomposition of biomass; this technology mainly includes liquefaction, combustion, gasification, pyrolysis and torrefaction [82].

1.6.2.1 Liquefaction:

Liquefaction is a high-pressure (up to 250 bars), oxygen-depleted thermal conversion process, which converts biomass into value added products such as biofuels and chemicals [83]. Due to the elevated reaction conditions, during the liquefaction process, chemical bonds within bio-polymers are broken, and monomers repolymerise into a variety of products (hydrocarbon oil). In general, liquefaction reduces the biomass oxygen content by releasing CO_2 and H_2O, thereby increase the calorific value of the final products [71]. Liquefaction is a relatively flexible biomass conversion technology. Because the process is performed in a solvent environment (usually water or an aqueous co-solvent system), no drying process is required beforehand, in contrast to other biomass conversion technologies, which usually require that the biomass has a relatively low moisture content [71]. In a previous study, it was reported that liquefaction could process biomasses that are comprised of up to 90% of moisture [84, 85]. In order to reduce the reaction temperature, time, and increase the selectivity, catalysts are commonly involved in the liquefaction process. The disadvantages of liquefaction technology are mainly focused on the limited biomass oxygen removal ability, which results in a hydrocarbon oil that is more polar compared to crude oil, and is

not suitable for substituting traditional petrol or diesel fuels [86]. Although the quality of liquefaction oil can be improved by subsequent hydrotreatment, the associated costs of the process will be increased accordingly [87].

1.6.2.2 Combustion

Combustion is the most direct and traditional biomass processing technology [88]. Basically, combustion is the burning of biomass in oxygen-rich conditions to convert the chemical energy that is stored in the biomass to heat or a combination of heat and power. Combustion is a series of chemical reactions that are performed to oxidize the carbon and hydrogen in biomass into carbon dioxide and water. The main combustion reactions are illustrated in Figure 18.

Combustion, as a simple biomass conversion technology that can be applied for many purposes, such as in a boiler, burner, internal combustion generators, etc. Via combustion, nearly all lignocellulosic biomasses and several animal-derived biomasses can be utilised for energy. Even though biomass combustion may produce pollutants such as nitrogen oxides, sulphur dioxide, carbon monoxide, and small particles, biomass combustion is still widely believed as being carbon neutral. Although promising, the biomass combustion also faces several problems.

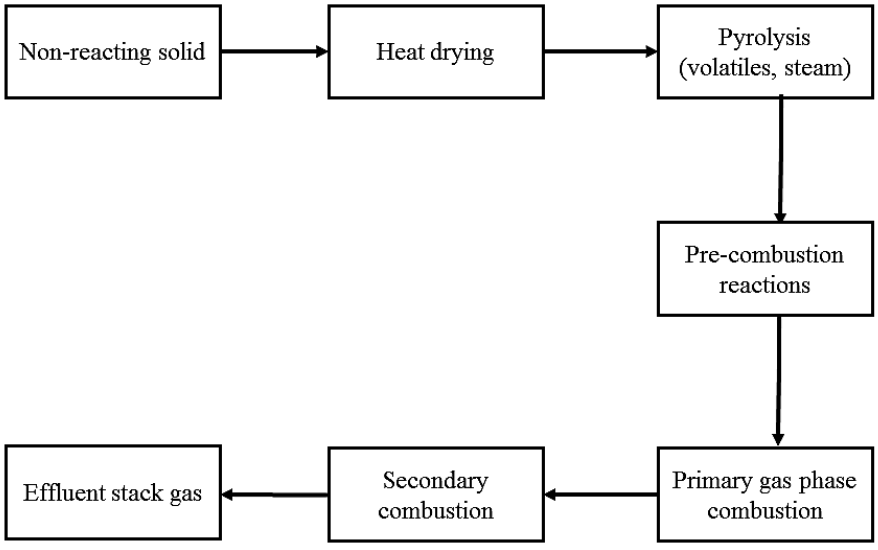


Figure 18: Major reactions in combustion process [89].

First of all, biomass generally has a lower physical and energy density than other types of fuels. When compared to coal, the calorific value of biomass is only about half [71]. The relatively high moisture content and low physical density make biomass facing challenges, such as insufficient combustion, high logistics costs, high storage costs, high pre-treatment costs etc. The toxic chemicals and particles that are released by directly burning biomass for energy can lead to serious environmental problems. Together, all those barriers make that cleaner, more efficient biomass conversion technologies to make fuels and chemicals, are desirable to meet the growing environmental concerns.

1.6.2.3 Gasification

Gasification is another biomass conversion technology, which converts biomass into syngas that mainly consists of CH_4, H_2, CO, and CO_2 [90]. The process is carried out by partially oxidizing biomass in the presence of oxidising agents and catalysts. Gasification is similar to combustion, however it is generally considered a partial combustion process [91]. A comparison between biomass combustion and gasification is listed in Table 4. By using the gasification process, biomass is converted into three major fractions: gas fraction (syngas as fuels), liquid fraction (hydrocarbon oils), and a solid fraction (chars). Normally, gasification takes place at an elevated temperature, which ranges from 700-1000°C. The high treatment temperature leads to a high gas yield (up to 85%) [92]. Syngas is commonly used as fuel and raw material for further chemical production, including production of methanol, dimethyl ether, ethanol, organic acids, and plastics [93].

Table 4: Comparisons between gasification and combustion [91, 94, 95].

Features	Gasification	Combustion
Purpose	Creation of valuable, environmentally friendly, usable products from waste or lower value material.	Generation of heat or destruction of waste.
Process type	Thermal and chemical conversion using no or limited oxygen.	Complete combustion using excess oxygen (air).
Raw gas composition (before gas clean-up)	H_2, CO, H_2S, NH_3, and particulates.	CO_2, H_2O, SO_2, NO_x, and particulates.
Gas cleanup	Syngas cleanup at atmospheric to high pressures depending on the gasifier design. Treated syngas used for chemical, fuels, or power generation. Recovers sulphur species in fuel as sulphur or sulphuric acid.	Flue gas clean-up at atmospheric pressure. Treated flue gas is discharged to the atmosphere. Any sulphur in the fuel is converted to SO_2 that must be removed using flue gas. Primarily consists of CO_2 and H_2O.
Solid by-products/products	Char or slag	Bottom and fly ashes
Ash/char or slag handling	Low-temperature processes produce a char that can be sold as fuel. High temperature processes produce a slag, a non-leachable, non-hazardous	Bottom ash and fly ash are collected, treated, and in most cases disposed as hazardous waste or can be sold as a material for

	material suitable for use as construction materials. Fine particulates are recycled to the gasifier. In some cases, fine particulates may be processed to recover valuable metals.	the preparation of concrete.
Pressure	Atmospheric to high	Atmospheric

1.6.2.4 Pyrolysis

Pyrolysis is a biomass thermal conversion technology, which decomposes biomass into gases, liquids, and solid residues by using heat in the absence of any oxidising agents. The gas fraction normally contains CO, CO_2, H_2, and CH_4. The liquid fraction is usually named "bio-oil", and contains hydrophilic organics (organic acids, alcohols), tars, and water [96]. Bio-oils are used as raw material for the production of bio-fuel and chemicals. The solid residue fraction, referred to as biochar, can be used as solid fuel or soil improver [97]. The pyrolysis process is generally classified into two categories: fast and slow by its heating regime, and the distribution of pyrolysis products largely depends on the operating condition. For example, a fast pyrolysis process at elevated heating rates and short residence times (< 1 s) produces up to 75 wt.% of liquid [98, 99]. However, a slow pyrolysis process is more favourable for the production of biochar. The classification of different types of pyrolysis is shown in Table 5.

Pyrolysis is a relatively clean and highly efficient biomass thermal conversion technology, and compared to direct combustion, products generated by pyrolysis have a much higher energy density and less hazardous emissions. A major advantage of the pyrolysis process is that it offers liquid products (bio-oils), which can be readily stored and transported [100]. Moreover, all three fractions of

pyrolysis products can be used as fuel, and the raw material for a further refinery or soil remediation. Thus, pyrolysis conversion is a high carbon economy process. Pyrolysis conversion also faces several barriers, among them, the most significant is the poor quality of bio-oil. Pyrolysis-generated bio-oils generally have a high water content, low heating value, incompatibility with conventional fuels, high viscosity, incomplete volatility, and are chemically instable [101, 102]. In order to make full use of bio-oil, purification and upgrading the process are required.

Table 5: Pyrolysis classification [103, 104].

Pyrolysis technology	**Process conditions**			**Products**
	Residence time	Heating rate	Temperature	Main Products
Very Slow(torrefaction)	Hours to days	Very low	300-500 ºC	Charcoal
Slow pyrolysis	Hours	Low	400-600 ºC	Liquid condensable vapour and gases
Moderate pyrolysis	5-30 min	<50ºC/min	400-600 ºC	Charcoal and gases
Fast pyrolysis	<1 s	~1000ºC/s	400-650 ºC	Liquid condensable vapor and char
Flash pyrolysis	<0.1 s	~1000ºC/s	650-900 ºC	Gases

1.6.2.5 Torrefaction

Torrefaction can be regarded as a prolonged pyrolysis process. However, unlike pyrolysis, the major purpose of torrefaction is to convert biomass into solid fuels (bio-chars), which have higher energy density, can easily be transported, and have

a better stability in comparison to bio-oils. The torrefaction technology effectively reduces the oxygen content in biomass, and thereby increases the energy content in biomass. Usually, the heating value can be increased from 10-17MJ kg^{-1} to 19-22MJ kg^{-1} with an energy densification ratio of 1.3 [71].

1.6.2.6 Bioconversion

Besides thermo-chemical conversion, biomass biological conversion provides another way of producing fuel and chemicals from biomass. In general, the bioconversion process involves fermentation and anaerobic digestion.

Bacteria and fungi are two commonly used microorganisms that are critical in the fermentation process. The purpose of fermentation is converting sugars into products such as fuels, chemicals, and biomaterials. Varies types of biomass feedstocks can be used for the fermentation process, however, traditionally starch-rich materials, such as corn and sugarcane) [105] are fermented to produce bioethanol. With the development of technology, more diverse biomasses, such as agriculture waste and food waste are used as feedstock for bioconversion, which helps lower the threshold and confliction to the food supply chain in biofuel production.

Prior to the fermentation process, biomass is usually pre-treated and hydrolysed in order to remove unfermentable fractions (lignin, minerals, etc.), which increases product yield.

1.6.3 Summary

Different biomass processing methods are introduced above. Heat is found to be one of the most important factors that may affect the efficiency and product distribution of the biorefinery process. Given this background, using a more controllable, efficient and selective heating method will potentially increase effectiveness of the biorefinery process. Due to the special heating mechanism,

microwave heating is considered to be one of the best alternative heating methods. More information about the microwave heating were provided in the following sections.

1.7 MICROWAVE TREATMENT

Microwave irradiation is essentially a type of electromagnetic irradiation with a frequency range of 0.3 to 300 GHz, and a wavelength range from 1 to 100 mm [106]. The microwave frequency range in the electromagnetic spectrum is shown in Figure 19. Microwave irradiation lies in between the radio and infrared spectra. Microwave technology is extensively used in RADAR transmissions, telecommunication, measurement and heating [107]. The application of microwave heating (radio frequency heating) was developed after World War II, and was introduced as a tool in chemical research in the 1980s [108, 109]. To avoid the interference with other uses, for the heating purpose, the microwave frequency was usually required to be locked in either 0.915GHz or 2.45GHz, with a wavelength of 333 mm and 12.2mm respectively [110]. In some extreme cases, microwave heating can be carried out at other frequencies within a proper shield with no radiation losses [108]. However, most of the domestic ovens are exclusively operated at 2.45GHz.

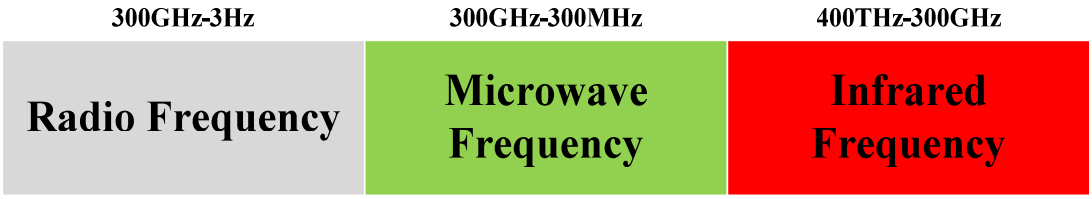


Figure 19: Radio frequencies of radio, microwave and infrared.

As a type of electrical volumetric heating, microwave heating can heat up all the infinitesimal elements that are present in the volume of a substance individually and ideally at the same rate. This property largely increased the efficiency of

heating due to “microwave dielectric heating effects” [111]. The comprehensive mechanism of how a substance absorbs microwave energy and converts it into heat is complicated and three major mechanisms are involved, including dipolar polarization (reorientation), ionic conduction, and interfacial (Maxwell-Wagner) polarization [112, 113].

Dipolar polarization is a microwave heating mechanism that works on substances that contain polar compounds. Under an electromagnetic field, the polar compounds form dipoles by displacing electrons and/or atomic nuclei from the equilibrium position. Those dipoles will attempt to rotate themselves to the applied electromagnetic field, a process that is known as reorientation. Because the electromagnetic field is oscillating at an enormously high frequency, reorientation of the dipoles occurs at a very high frequency. During this process, heat is generated by frictions between the polar molecules within the substance [106, 112]. In order to make the dipolar polarization heating effectively, the frequency of applied electromagnetic field should be moderate. If the frequency of the applied electromagnetic field is too high, there will be insufficient time for molecular rotation to take place, and therefore, no heating will occur. On the other hand, if the applied electromagnetic field frequency is too low, the molecular rotation would also be slow. Because the friction between molecules would not be intense enough, this will result in a reduced heating effect. The given exclusive microwave heating frequency lies perfectly in between these two extreme conditions; it is fast enough for the molecular dipoles to align with the applied electromagnetic field, but not too fast for the dipole molecules to follow.

Ionic conduction is another major microwave heating approach, which has a significant effect when the substance contains ions. Under microwave electromagnetic field, the charged ions and/or electrons will move through the

substance, thereby generating electric currents [112]. Under the oscillating electromagnetic field, those flowing ions and electrons intensively collide with each other, resulting in the generation of heat. In high electrical resistive materials, the ions and/or electrons are not allowed to flow freely, however the energy generated by the charged ions will still be dissipated in the form of heat [112].

Interfacial (Maxwell-Wagner) polarization is a special microwave heating technique that can be used for heterogeneous substances. In general, the conductivities and dielectric constants for heterogeneous substances are challenging. As a result, under microwave electromagnetic irradiation, charges will built up at the interfaces of different components and form polarisation, which may lead to heating effects [112].

This unique heating mechanism attracts much attention from chemists because the heating generation is largely dependent on the molecular properties. This allows for better control of the reaction and a potential control to the reactions' selectivity [113].

The ability of a substance to convert electromagnetic energy into heat is indicated by the loss factor (tan δ), which depends on two parameters, namely dielectric constant (ε') and the dielectric loss factor (ε"). The relation is expressed in the formula below:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

where, ε'' refers to the substance's efficiency of converting electromagnetic energy into heat, and ε' indicates the ability of molecules to be polarized by an electric field.

The loss factor (tan δ) is usually determined experimentally. A higher loss factor indicates that the substance is a better microwave absorber [114]. According to the value of the loss factor, common substances, in particular solvents that can be classified into high (tan δ > 0.5), medium (0.5 > tan δ > 0.1), and low (tan δ < 0.1) microwave absorbers [106].

The loss factor (tan δ) of several common solvents is listed in Table 6.

Table 6: Loss factor (tan δ) of selected solvents (under 2.45 GHz, at 20°C).

Solvent	**tan δ**	**Solvent**	**tan δ**
Ethylene glycol	1.350	Water	0.123
Ethanol	0.941	Chloroform	0.091
DMSO	0.825	Dichloromethane	0.042
Methanol	0.659	Toluene	0.040
Acetic acid	0.174	Hexane	0.020

1.8 MICROWAVE-ASSISTED BIOREFINERY

In the past few decades, microwave heating as an alternative heating method has attracted growing interests in the field of chemistry and in industrial production processes. Compared to conventional heating, the benefits of using microwave heating are presented in Table 7.

The benefits of microwave heating are the microwave's unique heating mechanism. In biomass thermal conversion processes, microwave heating has been introduced to many areas, such as biomass pretreatment [115], hydrothermal valorisation [116], and pyrolysis [117], and both at the laboratory scale and pilot scale [118].

Table 7: Advantages of using microwave heating in chemical reactions [106].

Category	Benefits
Higher reaction efficiency	Dramatically reduced reaction times
	Higher product yield
	Better reaction selectivity
	Cleaner reaction profiles Better energy efficiency
	Potential non-thermal microwave effects
Broader reaction medium selection	Broader choice of solvents (compared to conventional reflux setup) *
Better controllable	Better controllable reactors lead to more reproducible reaction conditions
	More adaptive to a parallel or automatic sequential processing format.

*The broader choice of solvents: instead of a given reaction that is limited by the boiling point, the dielectric properties of the reaction medium are more important for microwave-assisted chemical reactions.

Compared to conventional heating, microwave heating demonstrated a greater level of control and tunability. In some of the microwave-assisted treatment of biomass much lower temperatures are used, resulting in a significantly safer operating condition and reduction in costs [67]. Moreover, microwave-assisted hydrothermal treatment of biomass offers a different product stream and more efficient process, in particular for biomass with a high moisture content [67].

Overall, microwave heating is a "greener" alternative heating method. With the benefits of microwave heating mentioned above, it is possible to improve the biomass conversion process efficiency and selectivity, reduce costs and safety concerns, modify the distribution of products, as well as to achieve a better

controllability of the process. In some cases, microwave-assisted biomass conversion carries out reactions that are not possible to be conducted under conventional heating condition [106].

Chapter 2 Controllable production of liquid and solid biofuels by doping-free, microwave-assisted, pressurised pyrolysis of hemicellulose

Parts of the work described in this chapter has been published in:

"Controllable production of liquid and solid biofuels by doping-free, microwave-assisted, pressurised pyrolysis of hemicellulose." Energy Conversion and Management

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2.1 SUMMARY

Batch, pressurised microwave-assisted pyrolysis of hemicellulose in the absence of any external microwave absorber was found to be a promising route for the production of bio-based chemicals and biofuels. The experiments were conducted in a 10-mL batch reactor using a fixed power of 200 W employing different initial masses of xylan (0.1 - 0.7g) for a maximum time, temperature and pressure of 10 min, 250 ºC and 200 psi, respectively. The gas, bio-oil and solid (char) yields varied by 16-40%, 2-21% and 40-82%, respectively. Char production is preferential using a low amount of xylan (<0.25 g), whilst bio-oil production is favoured using a high amount of xylan (0.25-0.7 g). The effect of the sample mass is accounted for by the different physical state of the volatiles released during pyrolysis depending on the pressure attained during the experiment. This permits the process to be easily customised for the selective production of liquid (bio-oil) or solid (bio-char). Regarding the bio-oil, it is composed of a mixture of platform chemicals such as aldehydes, alkenes, phenols, polyaromatic hydrocarbons (PAHC), cyclic ketones and furans, with the composition varying depending on the initial mass of xylan. The char had a higher proportion of C together with a lower proportion of O than the original feedstock. Energy efficiencies of 100 and 26% were achieved for char and bio-oil production, respectively; thus leading to an increase in the HHV of the products (with respect to the original feedstock) of 52% for char and 19% for bio-oil.

Keywords:

microwave, pyrolysis, hemicellulose, bio-oil, bio-char

2.2 CHAPTER HIGHLIGHTS

- Microwave pyrolysis of xylan in the absence of any external microwave absorber
- High energy-efficient and controllable production of biochar and bio-oil from xylan
- Water in liquid phase is needed for fast microwave pyrolysis
- Production of bio-oil and bio-char with HHVs 52% and 19% greater than that of xylan

2.3 INTRODUCTION

2.3.1 Challenges in producing biofuels from lignocellulosic biomass

Renewable biomass as sources of chemicals and energy is set to increase with the excessive use and depletion of fossil fuels. In this context, the development of second generation biorefineries and utilisation of renewable resources, such as lignocellulosic biomass, is seen as one of the most efficient ways to achieve this goal [119]. Biofuels produced from lignocellulosic biomass have lower life-cycle greenhouse gas emissions compared to fossil fuels [120]. However, the utilisation of the lignocellulosic feedstock (LCF) is challenging due to both its diversity and variable cost (physical properties, chemical composition, collection logistics, etc.) [121]. This diversity creates challenges to develop replicable biomass supply systems and needs specialised conversion technologies to convert it to bio-power or biochemicals. The properties of LCF can be predicted based on a systematic investigation of the characteristics of the major biomass structural components, such as cellulose, hemicellulose, and lignin [122]. Cellulose and its decomposition have been well documented, whilst further investigation into lignin and hemicellulose pyrolysis is still challenging due to their more varied and complicated structure [123-125].

Hemicellulose is the second most abundant natural biopolymer after cellulose [126]. And xylan is the most abundant, representative hemicellulose [53]. Therefore, a detailed investigation into its properties will be essential for “modern zero waste” biorefinery processes.

2.3.2 Pyrolysis as a “tailor-made” route for biomass valorisation

Pyrolysis has been widely accepted as an attractive way to generate biofuels from biomass, a thermochemical conversion method [127]. During the pyrolysis of

biomass, it is well established that higher heating rates and higher final temperatures favour the production of gases and low molecular weight bio-oil fractions, while low heating rates and lower temperatures favour the production of char and higher molecular weight bio-oils fractions [128]; thus converting this process into a tailor-made route for the valorisation of biomass. However, the energy efficiency of this thermochemical route is one of its major issues for the development of this technology, and the efficiency of this heating method depends on the thermal conductivity and convection current of the material which converts it into a slow and low efficient process for the valorisation of biomass [127].

2.3.3 Additive free microwave assisted pyrolysis of biomass

Microwave irradiation has been shown to be a promising alternative to increasing the efficiency of the pyrolysis of biomass [129]. This method can provide energy efficient high rates of heating due to its controllability, selectivity as well as its non-contact and volumetric mechanism of interaction with the biomass [130]. This occurs due to the direct interaction of the microwave electromagnetic field with the ions and dipoles within the biomass source [106, 131, 132]. In particular, within the biomass, it is commonly assumed that water is the best microwave absorber [133, 134] and the dry vegetation relatively microwave passive [135].

A possible solution to overcome this limitation is the use of microwave absorbents, such as, activated carbon, graphite and silica carbide [136, 137]. Nevertheless, the addition of these types of external absorbents is a barrier to the industrial development. This impregnation not only is expensive but also it could create heterogeneous distributions within the biomass, resulting in the formation of 'hotspots', leading to non-uniform heating process and resultant unpredictable pyrolysis reaction mechanism [138].

Nevertheless, there are several publications that highlight the fact that the structural components of biomass alone and/or their products of decomposition are microwave active at high temperature. In particular, additive free microwave assisted pyrolysis of lignocellulosic feedstocks has been demonstrated for wood pellets [135], rice straw [139], corn stover [140], wheat straw [141] and rice husk [142]. Though, as these biomasses have different amounts of cellulose, hemicellulose and lignin along with some microwave active inorganics, the biomass structural compound or compounds responsible for the microwave activity of these feedstocks is not yet completely understood. Therefore, it is necessary to understand the behaviour of the biomass structural components alone to gain a depth insight into the microwave assisted pyrolysis of biomass.

2.3.4 Chanlleges in microwave assisted pyrolysis of biomass structural components

As stated above, there are a number of researchers have conducted studies on different biomass. However, the number of works studying the microwave assisted pyrolysis of biomass structural components alone is very limited. Specifically, there are only few works studying the microwave pyrolysis of cellulose and lignin, while the microwave pyrolysis of hemicellulose without any external microwave absorber has never been reported. Specifically, Farag et al. [143] analysed the microwave assisted pyrolysis of kraft lignin establishing a comparison between conventional and microwave heating with and without mixing the raw material with a microwave absorber. They found that microwave heating preserved the structure of the obtained products, improving the product selectivity. As regards the microwave assisted pyrolysis of cellulose, Al Shra´ah and Helluer [144] studied the effect of the temperature and the use of external microwave absorbers on the

product distribution and the properties of the bio-oil produced from microcrystalline and amorphous cellulose. It was found that an increase in the temperature resulted in an increase in the yield of bio-oil and gas along with a decrease in the biochar yield. While for microcrystalline cellulose higher yields of bio-oil and biochar and a lower yield of gas were obtained in a closed vessel system. Intrestingly, no significant differences were found between both setups when using amorphous cellulose. In addition, it was found that for amorphous cellulose the production of biochar and bio-oil was much greater at lower temperatures (< 220 ºC) than for microcrystalline cellulose due to the stronger intermolecular forces found for crystalline cellulose. This finding was previously reported by other authors [145].

Given this background, the following work addresses pressurised microwave-assisted pyrolysis of hemicellulose in the absence of any external microwave absorber. Different pressurised microwave-assisted pyrolysis experiments were conducted using both, constant microwave power and reaction volume, with various hemicellulose loadings. This permitted the analyses of how and to what extent the reaction pressure and the presence of pyrolysis decomposition products (which can act as good microwave absorbers) affect the microwave process efficiency and product selectivity. Bearing in mind that the absorber-free, microwave pyrolysis of hemicellulose has never been reported before, and the works dealing with the microwave pyrolysis of cellulose and lignin are scarce, this work represents a novel and challenging investigation not only for the valorisation of hemicellulose but also for the understanding of the behaviour of biomass under microwave heating.

2.4 MATERIAL AND METHODS

2.4.1 Materials and chemicals

Xylan extracted from beech wood (cell wall polysaccharide, >90% xylose residues), having a particle size ranged from 50 to 600 μm, was purchased from Sigma-Aldrich and used as received. Acetone (AR), deuterated acetone (Acetone-d_6) were both purchased from Sigma Aldrich and used as received.

2.4.2 Simultaneous Thermal Analysis (STA)

Mass loss and heat flow were measured using a Stanton Redcroft STA 625. Approximately 2.5 mg of xylan was added to an aluminium STA sample cup and then placed in the STA for analysis. The experimental conditions for the analysis were as follows: temperature 20 to 625 °C at 10 ºC min^{-1} in a 20 mL (STP) min^{-1} flow of nitrogen.

2.4.3 TG-IR analysis.

A thermogravimetric analyser (Netzsch STA-409 C/3/F) coupled to an FTIR spectroscopy (Brüker Equinox-55 FT-IR) via a narrow bore PTFE transfer line set at 180 °C, and a TASC 414/3 system controller was used to study the pyrolysis behaviour of xylan. The experiment was carried out at a heating rate of 10°C min^{-1} from 25 °C to 625 °C under a constant nitrogen flow of 100 mL (STP) min^{-1}. The volatiles released during pyrolysis were immediately transferred to the FTIR gas cell and analysed using a FTIR equipped with an MCT detector within the spectral range of 500-4000 cm^{-1} at a resolution of 4 cm^{-1}. The spectrum was recorded every 30 seconds.

2.4.4 Proximate and ultimate Analyses

Proximate analyses were performed according to standard methods (ISO-589-1981 for moisture, ISO-1171-1976 for ash and ISO-5623-1974 for volatiles). Elemental analysis based on carbon, hydrogen and nitrogen content was carried out using an Exeter Analytical (Warwick, UK) CE440 Elemental Analyser, calibrated against acetanilide with a S-benzyl-thiouronium chloride internal standard.

2.4.5 Xylan dielectric property with temperature.

The dielectric constant (ε') and dielectric loss factor (ε'') of xylan at 2.45GHz were measured by a cavity perturbation apparatus with temperature range from room temperature to 400 °C. A detailed description of the method can be found in the work of Robinson *et al*. [135, 146].

2.4.6 GC-MS

The bio-oils were solubilised in methanol, and the 1µl solution was injected in a Perkin Elmer Claus 500 gas chromatograph coupled to a Perkin Elmer Claus 560s mass spectrometer. A non-polar ZB-5HT (30m×0.25mm *id* × 0.25µm film thickness) column from Phenomenex (UK) was used. The oven temperature was maintained at 60°C for 1 min, then ramped at 10°C min^{-1} until 360°C and then held for 1 min. The NIST 2008 library was used for product identification.

2.4.7 2D-HSQC NMR analysis

The Heteronuclear Single-Quantum coherence (HSQC) 2D NMR spectra of the bio-oil products were analysed on a Bruker 400 MHz NMR spectrometer, whilst the spectra of bio-oil were qualitatively determined on a Joel 400 MHz spectrometer. The acetone used to extract the bio-oil was removed under vacuum. Approximately

100 mg of the extracted oil was then subsequently solubilized in 1.0 mL deuterated acetone (Acetone-d_6) ready for NMR analysis. HSQC experiments were performed using a 15 ppm sweep and 5ppm as the offset on ^{1}H- dimension, and 220 ppm sweep and 110 ppm as the offset on the ^{13}C-dimensions. For the ^{1}H-dimension, 1024 data points were used with an acquisition time of 64 ms, while 256 data points were used for the ^{13}C-dimension. The $^{1}J_{C-H}$ used was 145 Hz. In addition, 1.45 s pulse delay and 32 scans were also adopted. The acetone-d_6 solvent peak (δ_c 29.92 ppm and δ_H 2.05 ppm) was used for the chemical shift calibration.

2.4.8 SEM microscopy

SEM micrographs were recorded on a JEOL JSM-6469LV. Samples were Au/Pd coated on a high resolution sputter SC7640 at a sputtering rate of 1500V per min, up to a thickness of 7nm.

2.4.9 Microwave-assisted pyrolysis of xylan

A CEM Discover II (www.cem.com) microwave facility (shown in Figure 20) was used to carry out the pressurised pyrolysis experiments. This microwave reactor has a circular design of the waveguide, which focuses the microwave energy towards the reaction vessel; thus creating a highly uniform field of microwave energy in the centre of the cavity where the reaction vessel rests. This configuration provides consistent heating and the ability to rapidly heat up to the temperature of the experiment. In addition, this reactor has a ventilation and re-seal technology that allows releasing unexpected pressure quickly and safely thus minimising vessel failures.

The experiments were conducted in a 10 mL batch reactor using a fixed power of 200W employing different initial masses of xylan (0.1 - 0.7g) for a maximum time,

temperature and pressure of 10 min, 250 ºC and 200 psi, respectively. Close vessel and an open vessel configurations were used for this work. The close vessel reactor configuration retains the pyrolysis products (solid, liquid and gas) inside the reactor; thus increasing the pressure reached during the experiment. As this pressure depends on the mass of xylan used and the temperature achieved, different initial masses of xylan (0.1 - 0.7g) were used to analyse the effect of pressure on pyrolysis. Before the microwave power was initiated, the reactor vessel was filled with nitrogen to provide an inert environment, and the vessel subsequently sealed. During the experiments, the samples were irradiated under a fixed power of 200W for a maximum time of 10 minutes. In addition, extra experiments were performed under atmospheric conditions using an "open vessel configuration" to differentiate the effect of the system pressure and the presence of pyrolysis decomposition products in the process.

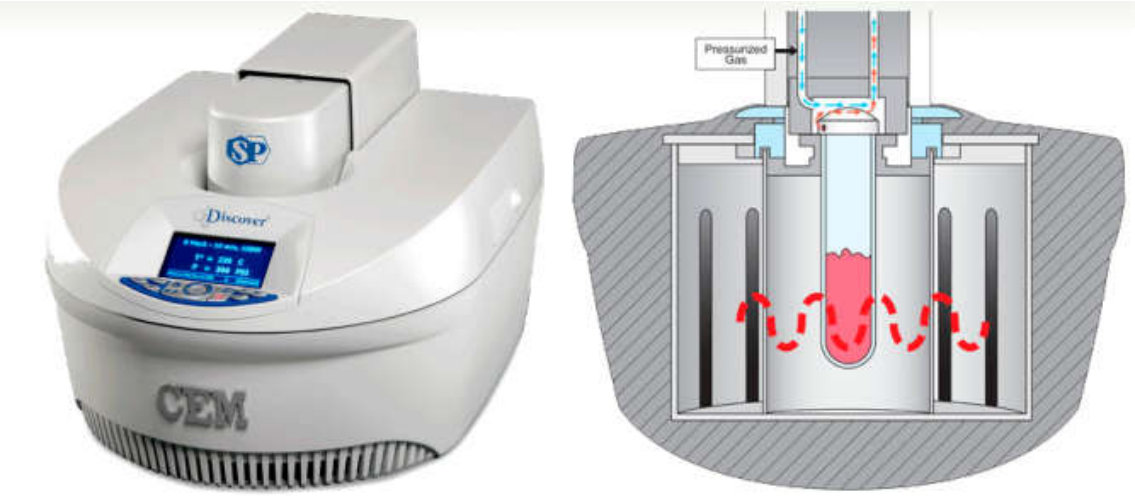

Figure 20: CEM-discover microwave.

2.5 RESPONSE VARIABLES AND STATISTICAL ANALYSES

The effect of the sample mass on the microwave-assisted pyrolysis was evaluated using different response variables (Table 8). These include the gas, liquid (bio-oil) and solid (bio-char) yields (%) together with the chemical (relative chromatographic area, %) composition of the bio-oil and the elemental (wt.%) analysis of the bio-oil and bio-char. One-way analysis of variance (one-way ANOVA) with the multiple range least significant difference (LSD) test, both with a significance level of 0.05, were used to evaluate the influence of the mass of xylan on the process.

Table 8: Response variables. Definitions and analytical techniques used in their determination for xylan.

Product	Response variable	Analytical method
Liquid	$\text{Liquid yield (\%)} = \frac{\text{mass bio} - \text{oil (g)}}{\text{mass of xylan (g)}} \times 100$	
	$\text{Composition (area \%)} = \frac{\text{area of each compound}}{\text{total area}} \times 100$	GC-MS (Gas Chromatography-Mass Spectrometry).
	$\text{C, H, O (wt. \%)} = \frac{\text{mass of C, H, O (g)}}{\text{mass of bio} - \text{oil (g)}} \times 100$	Elemental Analysis
	HHV (MJ/kg) = 0.3491 C (wt.%) + 1.1783 H (wt.%) – 0.1034 O (wt.%) – 0.015 N (wt.%) + 0.1005 S (wt.%)	Estimated [147]

Solid	Solid yield (%) $= \frac{\text{mass of solid (g)}}{\text{mass of xylan (g)}} \times 100$	
	HHV (MJ/kg)	Bomb calorimeter.
	C, H, O (wt. %) $= \frac{\text{mass of C, H, O (g)}}{\text{mass of solid (g)}} \times 100$	Elemental Analysis
Gas	Gas yield (%) $= 100 -$ Liquid yield (%) $-$ Solid yield (%)	

2.6 RESULTS AND DISCUSSION

2.6.1 Characterisation and thermal properties of xylan

The results of the proximate and ultimate analysis of xylan are listed in Table 9. These results are in good agreement with the characterisation results reported by other authors [148, 149]. Simultaneous thermal analyse (TG/DTA and TG-IR) of xylan (Figure 21 and Figure 22) was used to study the thermal decomposition and determine the thermal transitions and the reaction products (Figure 23).

Table 9: Ultimate and proximate analysis of xylan.

Proximate analysis (wt.%)	
Moisture	8.37±2.63
Ash	4.08±1.33
Volatiles	73.39±3.92
Fixed carbon	14.16±2.62
Ultimate analysis (wt.%)	
C	40.53±0.12
H	5.81±0.06
O*	53.66±0.16
LHV (MJ/kg)	15.45±0.10

* Oxygen was calculated by difference.

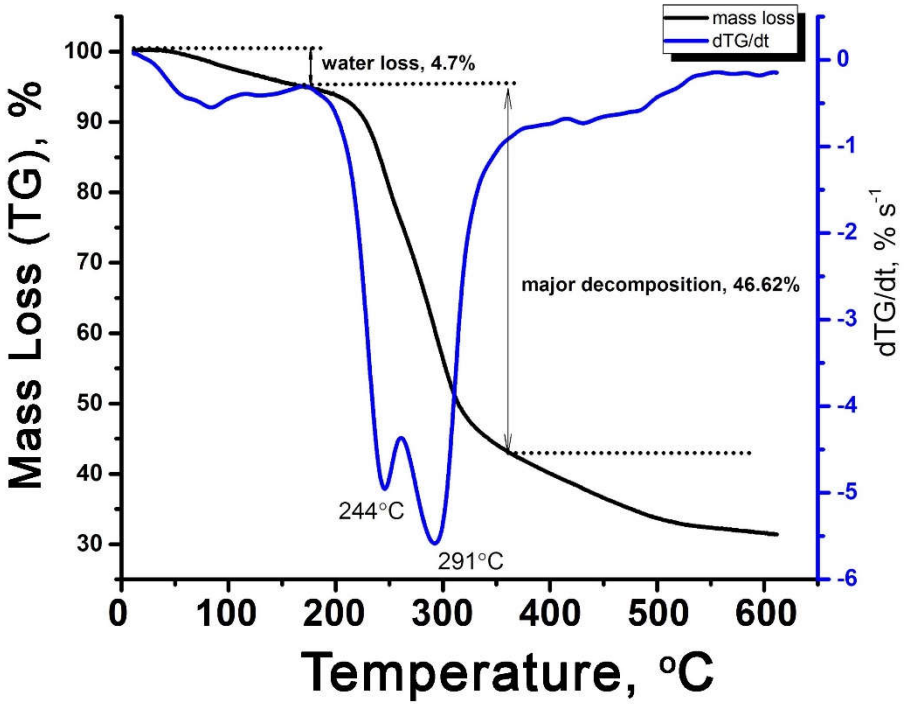

Figure 21: Xylan TG and differential thermogravimetric (dTG) analyses.

As regards the thermal properties of xylan, the evolution of the mass loss with the temperature (Figure. 21) shows three decomposition steps. The first step occurred at temperatures below 190 ºC, accounting for a 4.7% weight loss of the sample, which could be attributed to moisture content.

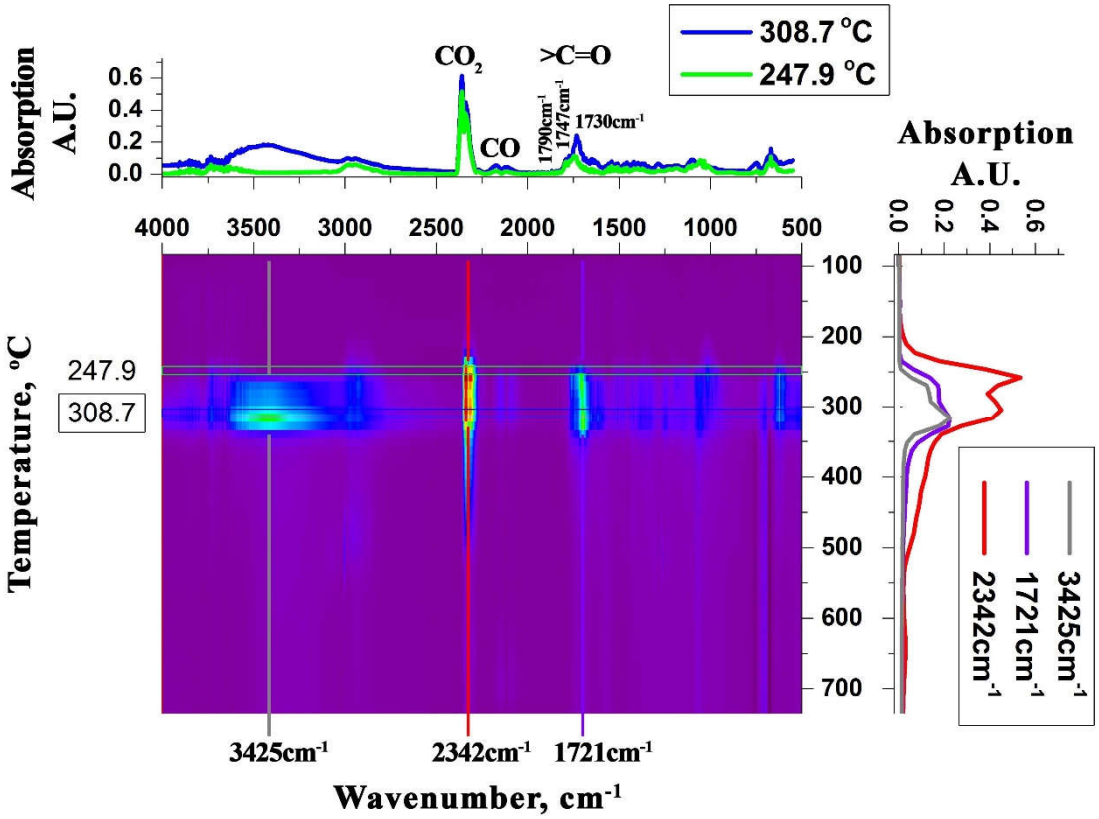

Figure 22: Xylan TG-IR data for conventional pyrolysis study.

The major degradation processes took place in the temperature range from 200 °C to 350 °C, with maximum rates of weight loss occurring at two stages: 244°C and 291°C, likely due to the heterogeneous structure of xylan. During this major decomposition phase (200-350 ºC), the mass loss accounted for about 47% and could be attributed to the thermal decomposition of xylan by means of dehydration, decarboxylation and decarbonylation reactions, among others. These results are in good accordance with the work conducted by Stefanidies et al. [150] who analysed the thermal decomposition of cellulose, hemicellulose and lignin under conventional heating.

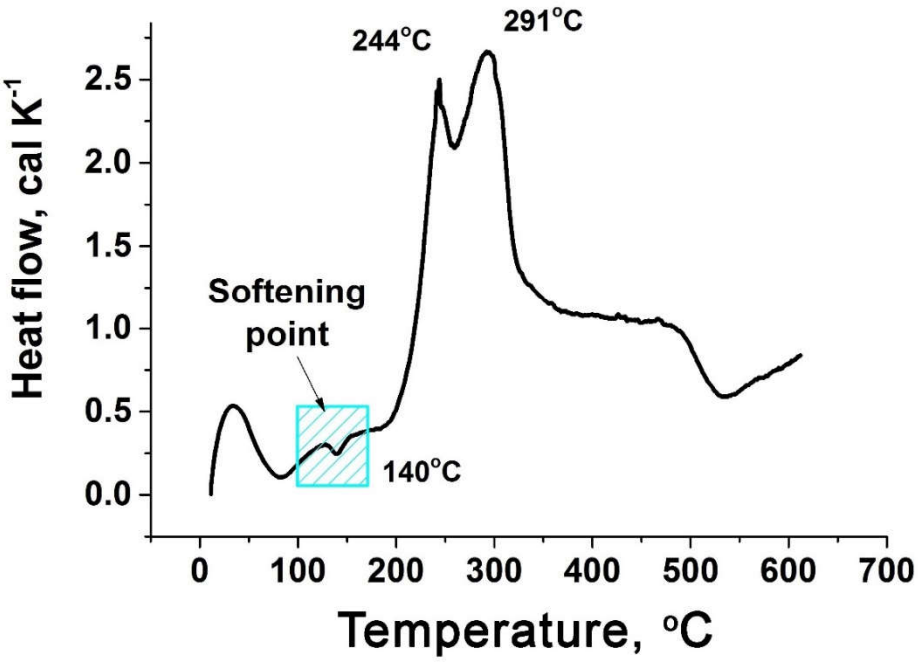

Figure 23: Xylan DSC information.

Xylan was sieved to produce two fractions: small (50-125 μm) and large (>500 μm) and the same thermal behaviour as reported for the original xylan was obtained for both fractions; thus suggesting that the thermal properties of the xylan used in this work are not affected by its particle size.

From the IR results, it was found that between 200 and 350 ºC CO_2, CO and H_2O are the major pyrolysis products (Figure 22). In addition, a characteristic band indicating the presence of C=O groups in the pyrolysis products was also observed. According to Wang et al. [151], this band suggests the formation of some of the following compounds: acetic acid, 1-hydroxy-2-propanone and/or furfurals from xylan. Over 400 °C, the rate of decomposition of xylan is reduced dramatically, due to the presence of resistant bonds in solid xylan residue. These maxima observed for the weight loss correspond to the two strong exothermic maxima at 245 °C and 290 °C shown in Figure 23. However, the other broad endothermic maximum at

low temperature within the range of 128-148 °C does not correspond to any significant mass loss or FTIR absorption and can, therefore, be associated with softening of xylan polymeric structure.

With respect to the dielectric properties of xylan, the relationship between loss factor (tan δ) at 2.45GHz and temperature is shown in Figure 24. From this analysis, it was observed that below 100 °C, xylan has a high loss factor, probably due to the presence of water, which is a common microwave absorber [115]. A further heating resulted into an inflexion in the tan δ curve at 140 °C, corresponding to the DSC softening point of xylan described above, and an increase in the materials microwave absorptivity. This softening of the structure will increase the flexibility of the xylan chains and the dielectric loss properties, thus promoting the interaction with the microwave field [115].

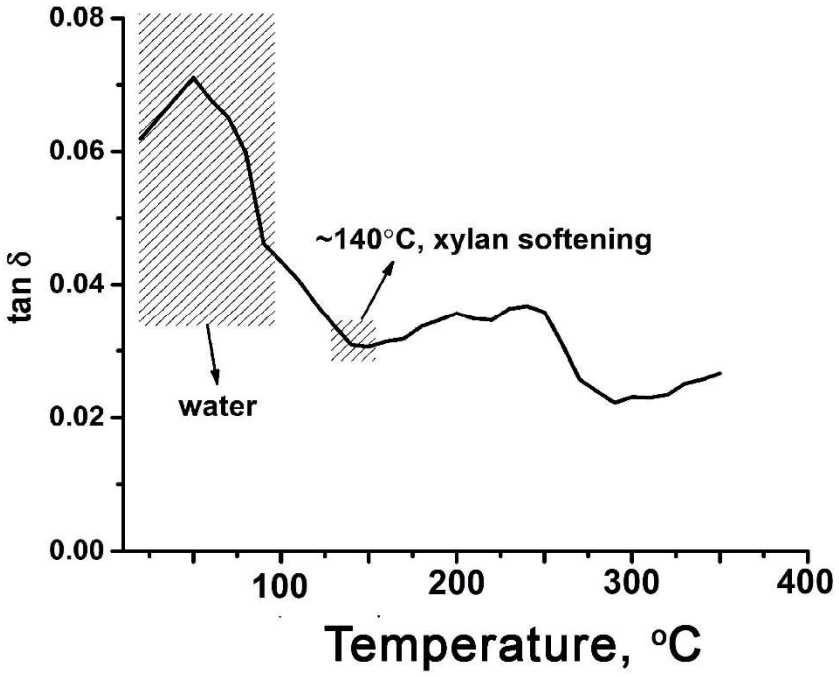

Figure 24: Xylan loss factors (tan δ) at 2.45GHz and temperatures from 25 to 350°C.

2.6.2 Global yields obtained in the microwave-assisted pyrolysis experiments

Figure 25 shows the yields of gas, liquid (bio-oil) and solid (bio-char) obtained during the microwave-assisted pyrolysis experiments with different initial xylan masses (0.1 - 0.7 g). The statistical analysis of the results reveals that the sample mass exerts a significant influence on the products distribution (p-value < 0.05). Specifically, the yields of gas, liquid and solid vary by 16-40 %, 2-21 % and 40-82 %, respectively.

Moreover, it was found that the sample mass does not exert a significant effect on the product distribution between 0.1-0.25 g. Within this interval a high amount of solid was produced in the pyrolysis process, thus minimising the yields of gas and liquid, resulting in a product distribution similar to that of torrefaction [98]. However, a further increase in the mass sample up to 0.7 g exerts two different effects: the first increase between 0.3 and 0.5 g leads to a sharp increase in the yields of gas and liquid together with a decrease in the solid yield. Similar trends were reported in the work of Al Shra´ah and Helluer [144] during the microwave-assisted pyrolysis of cellulose. Secondarily, a posterior increase between 0.5 and 0.7 g slightly decreases the yields of gas and liquid and increases the yield of solid. This last development is believed to be a consequence of the equipment limitation. The CEM-discover II microwave system has a safety temperature and pressure guard of 300 °C and 200 psi, respectively. Any reactions exceeding these limitations stop automatically. As a consequence, the pyrolysis reactions with a sample mass > 0.5 g were not fully carried out to completion.

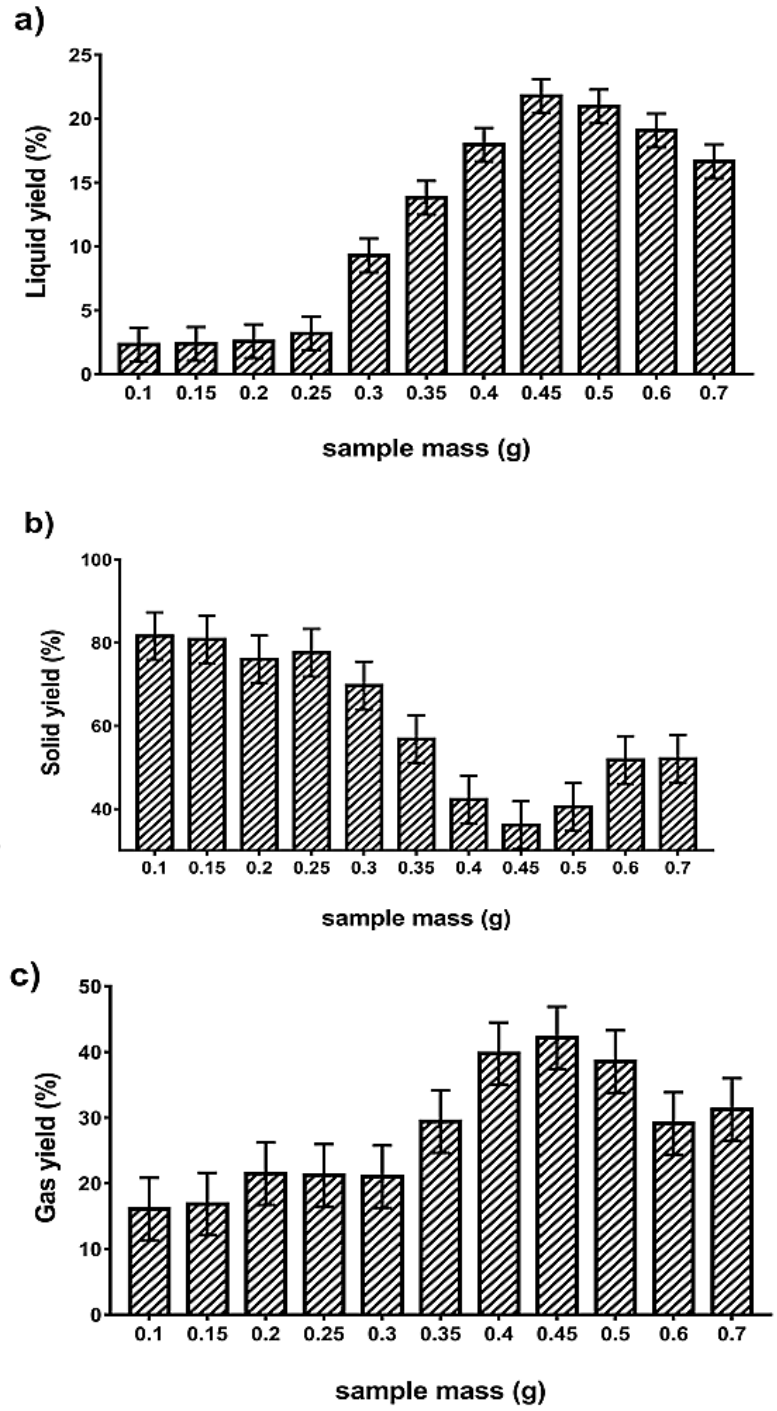

Figure 25: Overall product distribution. a) Liquid, b) Solid and c) Gas yield. Bars are LSD intervals with 95% confidence.

To gain a deeper insight into the effect of the sample mass on the pyrolysis results, pressure produced during pyrolysis was analysed. Pressure was selected as the

parameter to evaluate the reaction intensity during the pyrolysis reactions since the evolution of volatiles (condensable compounds), and gas generation are directly related. Figure 26 shows the evolution of the pressure as a function of the temperature for the different runs conducted. From the results plotted in Figure 26, two distinct developments can be observed. On the one hand, for the pyrolysis reactions with a relatively low sample mass (< 0.3 g), the maximum pressure achieved was less than 30 psi. On the other, reactions with initial sample mass greater than 0.3 g could reach pressures significantly higher, with rapid pressure build up during the process. These two different phenomena suggest the existence of two pyrolysis types depending on the pressure of the experiment: type I for mass samples between 0.1 and 0.25 and type II for samples 0.3 and 0.7 g.

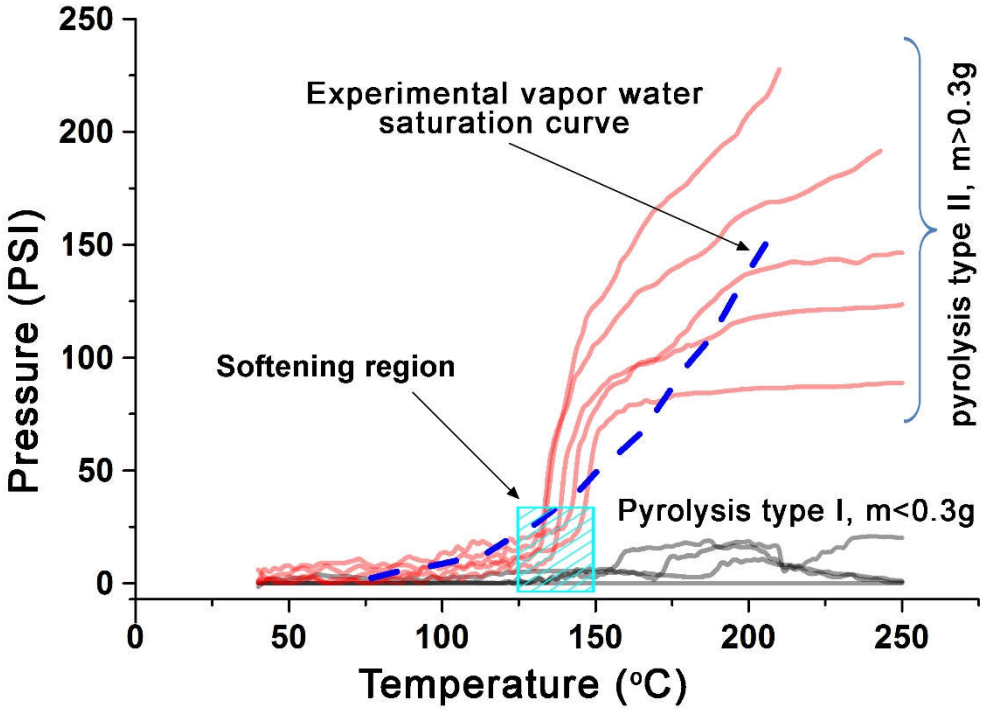

Figure 26: Relationship between pressure and temperature during the microwave heating of different sample masses of xylan.

It is believed that the development of one or the other pyrolysis type depends on the physical state (vapour or liquid) of the volatiles (water and/or other

decomposition products) released during the microwave assisted pyrolysis of xylan. In addition, it should be noted that according to the thermal profile of xylan (Figure 21), below 200 °C there is little decomposition of the material; therefore, pressure changes should be principally attributed to water. Comparing the experimental pressure-temperature curves obtained for the experiments with the vapour - water saturation curve (Figure 26), it can be found that for samples with a sample mass ≥0.3 g, the pressure generated during the reaction was high enough for the water released to be maintained in both the liquid and gas phase rather than only the gas phase. For these samples, significant pressure release was found between 138-150 °C, which coincides with the xylan softening point. The combination of increased chain mobility permitting better microwave absorptivity would aid release of bound water trapped within xylan [115]. For samples with a mass < 0.3 g, the pressure also increased slightly in the 138-150 °C region, but there was insufficient sample mass for the water released to be maintained at least partially in the liquid phase and was instead converted solely to vapour.

In order to investigate whether the volatiles trapped in the closed vessel caused the difference in reaction intensity, the heating rate was introduced as another parameter to evaluate the reaction intensity. This was carried out by comparing both the open (atmospheric pyrolysis) and closed reaction vessels (pressurised pyrolysis) using the same sample mass of xylan, as shown in Figure 27. For the 0.6 g experiment in the closed vessel, the heating rate in stage I was up to 6.36 °C s^{-1}, and 4.23 °C s^{-1} was achieved in stage II. However, the corresponding values were 1.50 °C s^{-1} and 0.60 ºC s^{-1} for the same mass in the open vessel system. This trend was also observed when loading 0.2 g of the sample as starting material. These results revealed the fact that the heating rate for the open vessel reaction system was significantly lower than that of the closed vessel reaction system. This development can be explained by the constant escape of the generated volatiles,

initially water (steam) and during pyrolysis, organics from the system. As water is the major microwave absorber in xylan, a lower moisture content would result in a lower sample tan δ and a poorer microwave interaction [115]. At the latter stages of the reaction, again with a low concentration of volatiles trapped within the reaction vessel, the lower loss factor (tan δ) of the samples would leads to slower pyrolysis, and furthermore, a different product distribution. Besides, acidic compounds generated from the decomposition process of xylan may act as a catalyst to promote this process in the closed vessel system [152].

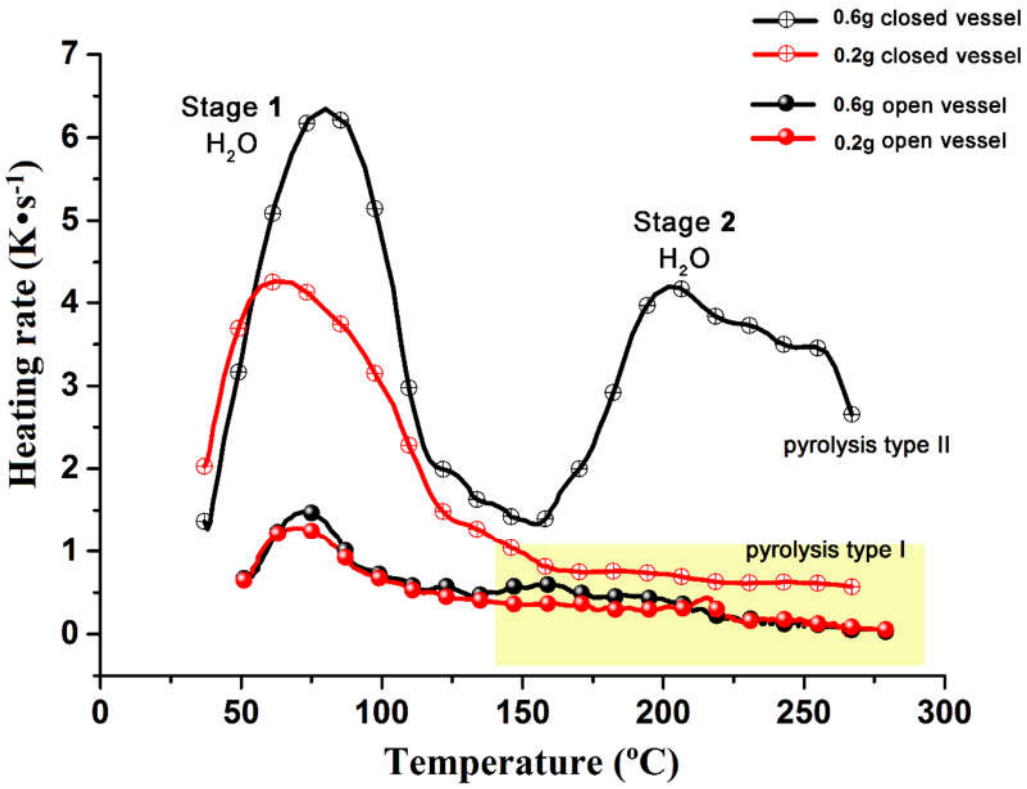

Figure 27: Heating rate and temperature relationship of comparable xylan sample masses heated under both open and closed vessels reaction systems.

The existence of these two pyrolysis types that depend on the pressure within the vessel, allows the process to be easily customised for the selective production of liquid (bio-oil) or solid (bio-char) product in a single reactor with minimum operational changes thus, aiding hemicellulose valorisation.

2.6.3 Bio-oil chemical characterisation

The chemical compositions of the bio-oils were experimentally determined by GC-MS, and a comparison was established between the liquids produced with different initial masses. It is known that the total amount of compounds present in the bio-oil that can be identified by GC-MS usually represents about 20 to 22 wt.% of the crude bio-oils [153], as many lignin-derived compounds cannot be analysed due to their high molecular masses. However, useful trends can be retrieved from this analysis, and a comparison can be established. Figure 28 lists the main compound groups that are present in the bio-oil: aldehydes (acetaldehyde and 3-furaldehyde), alkenes (1-butene, 4-ethoxy), phenols (methyl/di, ethyl/di and methoxy phenols such as phenol, 3-methyl, phenol, 3-ethiyl-5methyl, phenol, 2-ethyl, phenol 2,5-dimethyl, phenol 2,3-dimethyl and phenol, 2,6-dimethoxy), benzenes (1,2-benzenediol, 3-methyl and hydroquinone), polyaromatic hydrocarbons (PAHC: naphthalene, fluorene, phenanthrene, anthracene pyrene and fluoranthene), cyclic ketones (2-cyclopenten-1.one, 2-hydroxy-3-methyl; 2-cyclopenten-1-one, 3ethyl-2-hydroxy; 2-cyclopenten-1-one, 2-methyl and 1,2-cyclopentanedione, 3-methyl) and furans (2-furanmethanol and furfural). The bio-oil produced from xylan is rich in furans, aldehydes and ketones as expected due to the thermal decomposition of the xylan five-membered rings [150, 154]. The formation of the phenolic derivatives has been observed by other researchers as well, and may be attributed to further Diels-Alder or retro-Diels-Alder reactions between the furanic compounds and the aldehydes [150, 154] or to the decomposition of the remaining lignin side chains (impurities), acting as connections between the pure xylan and the lignin in the plant cell wall. Furthermore, mono-aromatic compounds can be formed from both furans and small-oxygenates by oligomerisation, decarboxylation and decarbonylation reactions. Poly-aromatic species can be produced as a final step from mono-aromatics [155, 156]. In addition, the presence of these compounds

in bio-oils is consistent with the results reported by Onwudili and Williams [157] and Remón et. al [158] for lignocellulosic bio-oil.

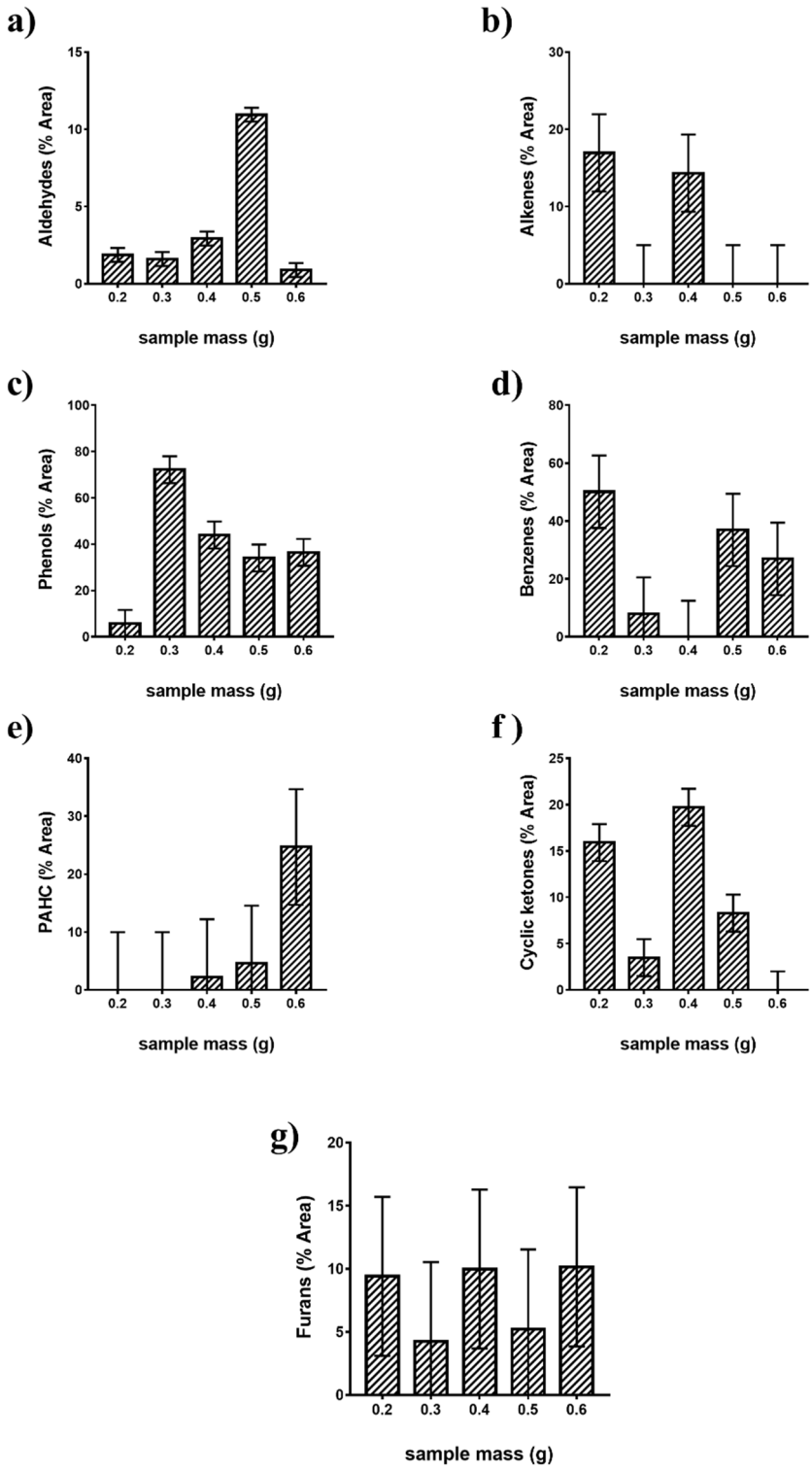

Figure 28: Bio-oil composition calculated as relative chromatographic area (%). Bars are LSD intervals with 95% confidence.

The statistical analysis revealed significant differences between the relative amounts of aldehydes, alkenes, phenols, benzenes, polyaromatic hydrocarbons (PAHC) and cyclic ketones. Conversely, variations in the concentrations for furans were not significant with 95% confidence. Regarding the effect of the pyrolysis conditions on the bio-oils chemical composition, similar trends to those reported above for the overall product composition can be observed in Figure 28. Specifically, for an initial xylan mass of 0.2 g (pyrolysis type I), the bio-oil produced is primarily made up of alkenes, benzenes, cyclic ketones and furans. Under these conditions the production of char from xylan is predominant. These results are in agreement with the work of Collard and Blin [159] who reported that the pyrolysis liquid from xylan is mainly aromatic, containing a significant amount of benzene rings. An increase in the initial mass of xylan placed in the reactor between 0.2 and 0.4g leads to an increase in the proportions of aldehydes, phenols along with a decrease in the relative amounts of benzenes, suggesting a further transformation of methoxybenzenes into phenols by a demethylation process [159]. A further increase in the sample mass up to 0.6 g of xylan leads to an increase in the proportions of PHAC and benzenes along with a decrease in the relative amounts of aldehydes, alkanes and cyclic ketones. These variations are believed to be the consequence of the shorter holding time used in the experiments as the reaction had to be stopped before completion.

In order to gain a greater insight into the chemical properties of the bio-oils produced under both low and high mass (type I and II) conditions, the liquids were characterised by heteronuclear Single-Quantum coherence (HSQC) 2D NMR. As regards the effect of the mass loading on the composition of the bio-oils, it can be observed that more peaks with stronger signal intensity could be identified for the greater initial mass (Figure 29) than for the lower mass loading (Figure 30)

experiments. This suggests that the pyrolysis conditions achieved with mass loadings greater than 0.3 g are more favourable for the decomposition of xylan. The δ_C/δ_H 60-85/3.0-5.5 quadrant corresponds to the aliphatic oligo-saccharides region overlapping with the region of the lignin-derived aliphatic side chain, which contains methoxyl groups, β-O-4' linkages (A), xylooligosaccharides structures and intermolecular linkages (C6 oiligosaccharides-A_γ) between xylooligosaccharides and lignin-like structures. The quadrant δ_C/δ_H 90-155/6.0-8.0 is commonly related to aromatics, where ferulic acid (FA) and other compounds with the guaiacol (G) unit, typically found in lignin, are observed [160, 161]. The existence of these compounds suggests that the xylan molecule tested (from beechwood) might also contain side chains common to lignin that can act as a connection between the pure xylan and the lignin in the plant cell wall.

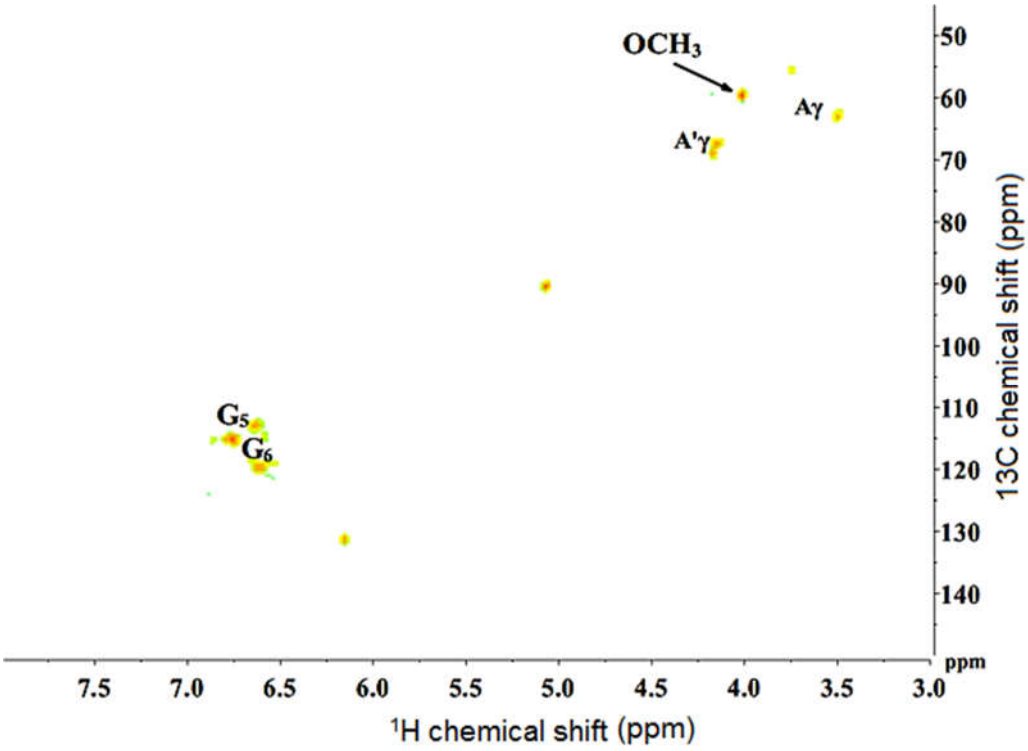

Figure 29: 2D HSQC NMR spectra of the xylan pyrolysis oil fractions: Bio-oil produced from low initial sample mass (0.2 g) experiments.

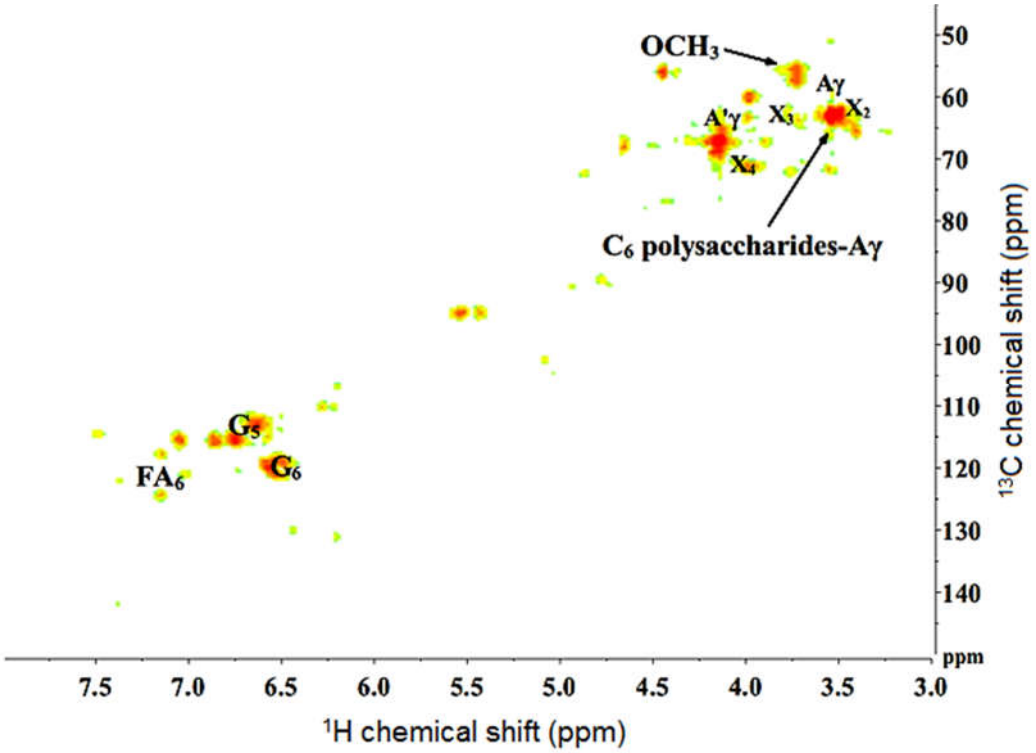

Figure 30: 2D HSQC NMR spectra of the xylan pyrolysis oil fractions: Bio-oil produced from high initial sample mass (0.5 g) experiments.

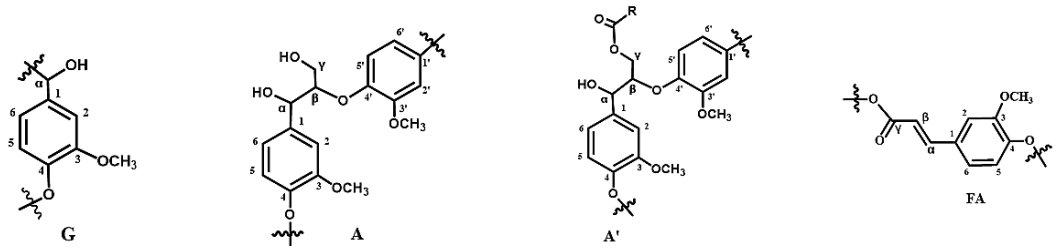

Figure 31: The structure of potential functional group.

Therefore, the sample variation in the bio-oils derived from different initial sample masses can be ascribed to the different heating rates they were subjected to. Based on the 2D-HSQC results, the absence of signals related to xylooligosaccharides in Figure 29 indicates that the reaction intensity was not high enough under low heating rate conditions (type I) to cleave the bonds between the xylan monomers, but sufficient to break the xylan-lignin bonds. Therefore, from this analysis it can

be seen that the bio-oil from low initial sample mass experiments mainly contains water and some acetone-soluble lignin compounds, corresponding with the thermal decomposition of the lignin fraction attached to the xylan structure. In contrast, the bio-oil produced using a high initial sample mass (above critical mass) contains both xylooligosaccharides peaks and lignin-like species indicating that the reaction intensity was high enough (type II) to break the bonds between xylan and the lignin and even the bonds between the xylan monomers. Depolymerisation of the lignin fraction present in xylan yielding alkyl phenols [162] may also explain the increase in the proportion of methoxy phenolic compounds in the bio-oil when increasing the initial mass as showed above. It is considered that the lower pyrolysis heating rate might have a selectivity to the cleavage of intermolecular linkages between lignin and the xylan backbone since the lignin-xylan linkages have weaker bond energies than the intramolecular bonds [163].

In addition, the bio-oil produced using 0.5 g of xylan was characterised using elemental analysis and its HHV was estimated. The elemental analysis (wt.%) of the produced liquid is as follows: 47.61 ± 0.52 C, 5.64 ± 0.28 H and 46.75 ± 0.81 O, which leads to HHV of 18.44±0.60 MJ/kg.

2.6.4 Bio-char chemical characterisation

Table 10 shows the elemental analysis and respective HHV for the original feedstock (xylan) and the chars produced using conventional pyrolysis and microwave (type I, low mass) and (type II, high mass) pyrolysis.

Table 10: Elemental composition and HHV for xylan, the char produced under both type I (0.2 g) and II (0.5 g) microwave pyrolysis types respectively, and the char produced under convection heating conditions. Results are presented as mean ± standard deviation.

	Xylan	0.2 g Char [a]	0.5 g Char [a]	Char [b]	p-value
C (wt.%)	40.53±0.12^{D}	59.44±0.02^{B}	61.75±0.40^{A}	47.49^{C}	<0.0001
H (wt. %)	5.81±0.06^{A}	4.31±0.08^{B}	4.58±0.18^{B}	5.50^{A}	0.0033
O (wt.%)*	53.66±0.16^{A}	36.20±0.055^{C}	33.72±0.17^{D}	47.01^{B}	<0.0001
HHV (MJ/kg)	15.45±0.10^{C}	22.08±0.10^{A}	23.47±0.33^{A}	19.61^{B}	<0.0001

[a] Microwave; [b] Conventional heating at a heating rate of 0.5 K s^{-1} up to 270°C

* O was calculated by difference.

A, B, C and D in each row are statistically different groups with 95% confidence.

The statistical analysis of the results reveals significant differences in the elemental analysis and the HHV between the original material and the three types of char considered (p-value < 0.05). Specifically, the three chars have a higher proportion of C together with a lower proportion of O than the original feedstock, which leads to a considerable increase in the HHV of the solids produced in comparison with the HHV of xylan. Conversely, while the proportion of H in the char produced with microwave pyrolysis decreases, significant differences are not found between the original feedstock and the char produced under conventional pyrolysis. Concerning the effect of the type of heating, both chars produced using microwave heating have higher and lower proportions of C and O, respectively, than that produced using conventional heating. This accounts for the statistically higher HHV of both solids in comparison with both, the original material and the char produced by conventional pyrolysis; thus, highlighting the effectiveness of microwave heating for the valorisation of xylan. In respect to the effect of the microwave pyrolysis type on the elemental analysis of the chars, a solid with a lower proportion of C and a greater proportion of O was produced under slow microwave heating.

To gain a better insight into the differences observed for the different chars, the atomic H/C and O/C ratios were calculated and these values were compared using

the Van Krevelen (VK) diagram (Figure 32). In addition, different biomasses and carbonaceous materials were added to the diagram for comparison purposes. From the change in the atomic O/C and H/C ratios, the slopes in the VK diagram can be theoretically calculated. For example, if a thermal process proceeds purely via dehydration, decarboxylation or demethylation, the gradient change in this diagram would be 2.2, -1.4 and -3.9, respectively. Therefore, comparing the H/C and O/C ratios for the conventional char sample with those for xylan, a gradient of 1.27 is calculated, which indicates that degradation proceeds mainly via dehydration. The comparison between the chars produced with microwave heating reveals that the samples produced under both pyrolysis types have a gradient of 1.49 and 1.69, respectively. This development indicates that the pyrolysis type II sample has a decarboxylation/dehydration ratio slightly higher than that produced under slower heating rate conditions.

Though, in both cases, the extent of pyrolysis is significantly more advanced than the conventionally heated sample with dehydration promoted to a greater extent with microwave heating. Regarding the use of these solid materials as a bio-fuel, the composition of the conventionally heated sample, still lies within the biomass range of materials. Though, the microwave produced chars clearly can be placed with samples more consistent to peat, emphasising the improvement in calorific value. The dehydration and decarboxylation reactions can enhance the properties of biomass by reducing the hydrogen and oxygen contents of biochars, resulting in an increased calorific value [164].

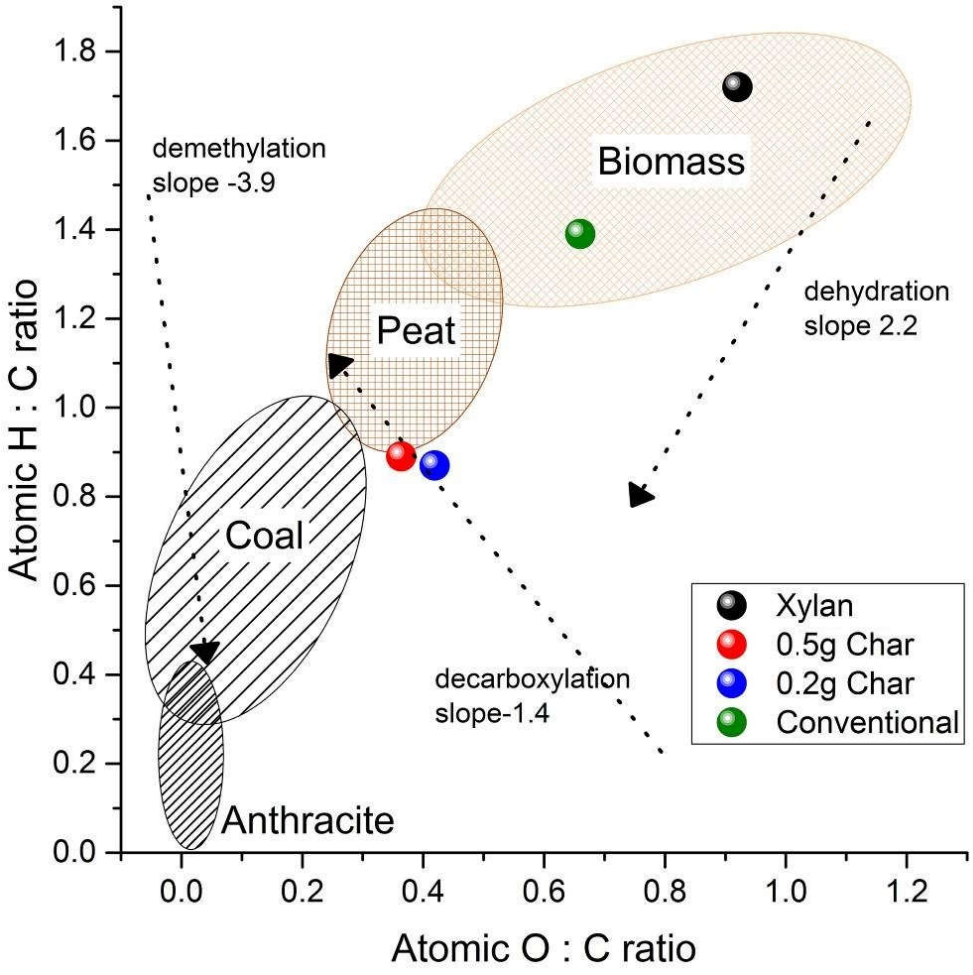

Figure 32: Van Krevelen diagram adapted from McKendry, [165] showing the H/C and O/C atomic ratios for several solid fuels and the comparative ratios for Xylan, and the bio-chars produced under convection heating and microwave heating with different masses.

2.6.5 Energetic assessment

To analyse the suitability of using the char and bio-oil produced from xylan for energetic purposes, the energy efficiency [166] of the process and the improvement in the HHV of both products compared to the initial feedstock were calculated. Table 11 shows the calculations for the char and bio-oil obtained employing the optimum microwave-assisted pyrolysis conditions: 0.2 g and 0.5 g of xylan, respectively.

Table 11: Energetic assessment for optimum conditions to produce char and bio-oil: energy efficiency and HHV improvement. Results are presented as mean ± standard deviation.

	Char	**Bio-oil**
Yield to product	75.97 ± 3.43	20.96 ± 0.63
HHV (MJ/kg)	22.08 ± 0.10	18.44 ± 0.60
Energy efficiency (%)	100 ± 3.43	26.06 ± 3.78
HHV improvement (%)	52 ± 0.09	19 ± 4.93

The energetic calculations listed in Table 11 shows that the microwave-assisted pyrolysis of xylan leads to an increase in the energetic density of the products. Specifically, energy efficiencies of 100 and 26% were achieved for char and bio-oil production, respectively; which leads to an increase in the HHV (with respect to the original feedstock) of 52% for char and 19% for bio-oil production. The lower energy improvement obtained for the bio-oil in comparison to the char is believed to be a consequence of the equipment limitation. As explained before, all the reactions exceeding temperature and pressures greater than 300°C and 200 psi were stopped due to equipment safety precautions. Therefore, higher bio-oil yields could have been achieved employing greater pressures and more research is still needed to maximise the process towards the production of an energy-rich bio-oil product. This suggests that more investigation is needed to develop new microwave-assisted pressurised reactors capable of achieving high pressures for the valorisation of hemicellulose towards an energy rich bio-oil. In addition, more investigation on the

effect of the xylan particle size and/or the presence of impurities could be beneficial for the scale-up and/or commercialisation of this technology.

2.7 CONCLUSIONS

This chapter addresses the pressurised microwave-assisted pyrolysis of hemicellulose in the absence of any external microwave absorber as a promising route for the production of biofuels from biomass. The most important conclusions obtained from this study are summarised as follows.

1. Sample mass exerted a significant influence on the product distribution. The gas, bio-oil and solid (char) yield varied by 16-40 %, 2-21 % and 40-82 %, respectively. Specifically, solid production is favoured using a low amount (0.1-0.25 g) of hemicellulose. This resulted in up to 80% conversion of the feedstock into char; thus, minimising the yields of gas (20 %) and bio-oil (3 %). Conversely, a further increase in the amount of hemicellulose from 0.3 to 0.7 g led to a sharp increase in the yields of gas (40 %) and bio-oil (20 %) together with a decrease in the char yield (40 %).

2. The effects of the mass loading accounted for by the different physical state (vapour or liquid) of the volatiles released during the pyrolysis reaction depend on the pressure reached in the experiment. This different pressure allowed the development of two different pyrolysis types. While a low pressure (<30 psi) was generated with mass loadings lower than 0.3 g (pyrolysis type I), a substantial increase in pressure (30-170 psi) occurred with hemicellulose loadings between 0.3 and 0.7 g (pyrolysis type I).

3. Characterisation of the bio-oil by GC-MS revealed that it was made up of aldehydes, alkenes, phenols, polyaromatic hydrocarbons (PAHC), cyclic ketones

and furans, having a composition dependent on the mass of hemicellulose employed. Use of 2D-HSQC to characterise the bio-oils revealed that the liquid produced from low initial mass sample experiments (pyrolysis type I) was made up of lignin-derived compounds obtained from the decomposition of the lignin fraction attached to the xylan structure. In contrast, the bio-oil produced using a high initial mass sample (pyrolysis type I) contained both xylooligosaccharides and lignin-like species indicating that the reaction intensity was high enough not only to break the bonds between xylan and the lignin, but also the bonds between the xylan monomers.

4. The solid product (char) has a higher proportion of C together with a lower proportion of O than the original feedstock, which leads to a considerable increase in its HHV in comparison to xylan. In addition, the char produced using fast heating had a decarboxylation/dehydration ratio slightly higher than that produced under slower heating rate conditions.

5. Energy efficiencies of 100 % and 26 % were achieved for char and bio-oil production, respectively. This led to an increase in the HHV (with respect to the original feedstock) of 43 % for char and 19 % for bio-oil production. The lower energy improvement obtained with bio-oil compared to that of the char is believed to be a consequence of the equipment limitation.

Chapter 3. A novel "bamboo-refinery" concept: selective bamboo fractionation by means of a microwave-assisted, acid-catalysed, organosolv process

Parts of the work described in this chapter has been published in:

"Towards the development of a novel 'bamboo-refinery' concept: Selective bamboo fractionation by means of a microwave-assisted, acid-catalysed, organosolv process." Energy conversion and Management

T. Li, J. Remón, Z. Jiang, V.L. Budarin, J.H. Clark

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York, United Kingdom, April 2017

3.1 SUMMARY

This work addresses a novel microwave-assisted, acid-catalysed, organosolv (EtOH/H_2O) system for the selective fractionation of bamboo, examining the effects of the temperature (110-190 ºC), solvent system (EtOH/H_2O) and catalyst amount (0-5 vol.% formic acid) on the process. A schematic showing of this process is illustrated in Figure 33. The statistical analysis of the results revealed that the operating variables exert a significant influence on bamboo fractionation, allowing the selective production of i) a cellulose-rich solid fraction, ii) a hemicellulose rich water-soluble fraction and iii) a lignin rich solid fraction. The yields of each of these fractions varied between 51-94%, 2-23% and 2-32%, respectively. Increasing temperature exerted a positive effect on bamboo decomposition, increasing the overall bamboo conversion and influencing the effect that the solvent system (EtOH/H_2O) has on the process. At low temperature (110 ºC) the solvent system does not have much influence, while a synergetic interaction between EtOH and H_2O took place at higher temperatures, which allowed better results to be obtained with EtOH/H_2O mixtures than with the pure solvents alone. The effect of the catalyst was relatively weak, being greatest when using a high temperature (190 ºC) and high proportions of water (>85 vol.%) in the solvent system. With respect to the properties of each fraction, the cellulose rich solid fraction was made up of un-reacted cellulose (44-83 wt.%), hemicellulose (0-21 wt.%) and lignin (12-34 wt.%); the water-soluble hemicellulose rich fraction consisted of a mixture of oligomers, sugars, carboxylic acids, ketones and furans; and the solid rich lignin fraction comprised high purity (>95 wt.%) organosolv lignin. The optimisation of the process revealed that by using a temperature of 190 ºC, a solvent system consisting of 45 vol.% EtOH and 55 vol.% H_2O with a concentration of formic acid of 5 vol.% it is possible to fractionate bamboo into a high purity (84 wt.%) cellulose solid

fraction, very pure (>95%) organosolv lignin and a rich water-soluble hemicellulose fraction consisting of a mixture of oligomers (27 wt.%), sugars (56 wt.%) and carboxylic acids (14 wt.%); thus converting this process into a very promising method for the selective fractionation of bamboo.

Keywords: microwaves, bamboo, organosolv, biomass fractionation, biorefinery

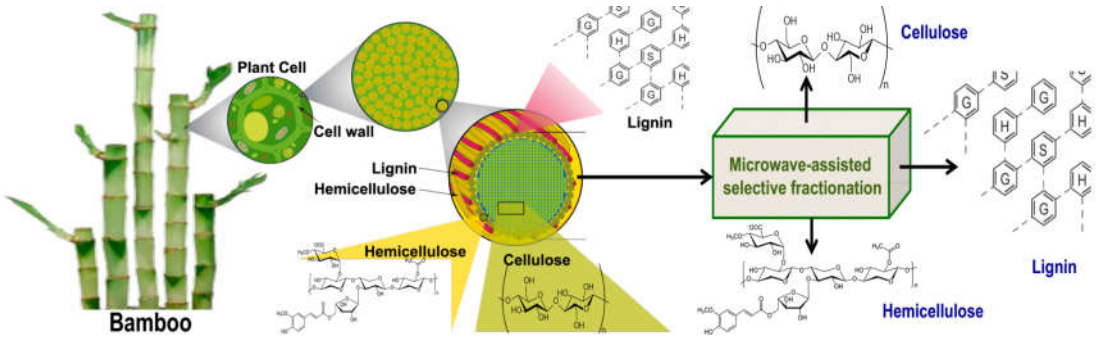

Figure 33: Schematic microwave assisted bamboo fractionation.

3.2 CHAPTER HIGHLIGHTS

- Microwave-assisted bamboo fractionation into cellulose, hemicellulose and lignin
- Analysis and optimisation of the temperature, EtOH/H_2O system and catalyst amount
- Synergetic effect between EtOH & H_2O during bamboo fractionation at high temperature
- Optimum conditions for bamboo fractionation: 190 ºC, 45% EtOH/H_2O and 5 vol.% HCOOH

3.3 INTRODUCTION

3.3.1 Bamboo, a fast growing, non-food biomass for biorefinery.

Throughout the world new policies to mitigate global climate change have led researchers to seek new processes, alternative renewable materials and more sustainable strategies to replace the current petroleum-based energy industry with a greener and more environmentally-friendly energy market. As part of this, the bio-refinery concept is gaining increasing attention, as biomass is the only renewable source of carbon that can be converted into gas, liquid and solid products [167]. Unfortunately, the development of a lignocellulosic biorefinery has received some criticism, since energy and chemical production in this way could affect the food supply and total forestry area. To overcome this issue, researchers are looking for fast growing and low "food-conflict" biomasses.

Among all the potential biomass feedstocks, bamboo is regarded as an excellent candidate. Bamboo is a big wooden plant, which is widely distributed in subtropical temperature zones around the world (latitudes from 46°N to 47°S) [168]. As one of the fastest growing woody plants, bamboo can grow at a rate of 30-60 cm/day to 15-40 m with a culm diameter of 30 cm [168, 169]. Due to its fast-growing property, bamboo generally could produce a higher yield of biomass than other common crops [170]. Typically, bamboo contains 37-47 wt.% cellulose, 15-30 wt.% of hemicellulose and 18-31 wt.% lignin, depending on the species [170]. In the past, bamboo was widely cultivated in Asian countries and used as a raw material for food, handicrafts, paper and construction. In recent years, bamboo has shown a huge potential to be used for the production of biofuel and other value-added chemicals via bioconversion [170-173].

3.3.2 Organosolv as a pretreatment method for bioconversion

Bioconversion is believed to be one of the most attractive methods for lignocellulosic biomass utilisation; enzymes and bio-catalytically active cells (fermentation) being the two pathways commonly employed [174]. This biotechnology is mainly used for bioethanol, biodiesel, biobutanol, methane and fine chemicals production [175]. In the past few years, bioconversion technology has undergone dramatic growth, which has increased the attention of researchers and industry. Nevertheless, the intrinsic complexity of biomass hampers the development of this technology, and more research is needed. In particular, within the lignocellulosic biomass structure, cellulose and hemicellulose are intimately associated with lignin in the cell wall, and part of the cellulose is in crystalline status. This hinders enzymes and microbes from achieving biomass digestion and, therefore, the pre-treatment of biomass for its selective fractionation into its main constituents (cellulose, hemicellulose and lignin) is still a challenge.

In the midst of the different strategies for biomass fractionation, the use of water/organic solvent (organosolv) processes is gaining increasing attention. Several works have been conducted with rice straw [176], cotton stalk [177], wheat straw [178-180], hemp hurds [181, 182], corncob [160, 183], maple wood [184], reed [185], corn stover [186] and bamboo [187, 188]. This route is well known for its higher efficiency in removing lignin under acidic condition than other processing methods. Organosolv systems can be classified into two categories: pure organic (simple) and aqueous-organic solvent (multiple) systems. In general, aqueous-organic systems perform better than single solvent systems [189, 190]. The multiple systems consist of a nucleophile agent (H_2O, in the vast majority of the cases, to react with the activated linkages in biomass) and an organic solvent to help dissolve the liberated fragments [191]. This water/organic mixture exerts a significant

influence on biomass depolymerization kinetics and thermodynamics, which affects not only the solubility of biomass but also the dissolution of biomass-derived products. This is of particular interest for the solubilisation of lignin which has both nonpolar and polar functional groups [192]. In addition, a homogeneous acid catalyst is used in some cases to increase the kinetics of biomass depolymerization in organosolv systems and, therefore, help increase the overall efficiency of the process.

Regarding the organic compounds used in H_2O/co-solvent systems, alcohols are the most commonly used as they have a low boiling point and can efficiently fractionate biomass into relatively high purity lignin and cellulose for further applications [193]. In particular, Hu et al. [194] regarded the H_2O/ethanol organosolv system catalysed by oxalic acid as one of the greenest co-solvent systems for biomass fractionation. They reported that by using this orgnaosolv system and employing a temperature of 140°C and a pressure of 2MPa for 1h, it was possible to recover 88 wt.% of the hemicellulose and 89 wt.% of the lignin present in corn stover, the cellulose remaining in the solid residue. Quignard et al. [180] worked on the extraction of lignin from wheat straw by using a H_2O-ethanol organosolv system at 160°C for 2h, examining the effect of different homogeneous Lewis acidic catalysts, such as $FeCl_2$, $CuCl_2$, $FeCl_3$, $Ga(OTf)_3$, and $ZrOCl_2$. It was found that lignin extraction was related to the acidity of the catalyst, with a maximum of 80% lignin conversion. Methanol has also been used in water-organic systems. In particular, Shimizu and Usami [195] used a catalysed (0.2 wt.% of HCl) methanol/H_2O mixture at 170 ºC for 45 min to fractionate pine wood, achieving very high hemicellulose (100%) and lignin (90%) recoveries. In addition, high boiling point alcohols, such as ethylene glycol and glycerol, have also been tested in the presence of H_2O for organosolv processes. This allows a low-pressure treatment to be

conducted, but hinders solvent removal; thus decreasing the energy efficiency of the overall treatment [193].

Besides alcohols, other organic solvents have also been tested with positive results for biomass fractionation. For example, the H_2O/γ-valerolactone (GVL) co-solvent system was positively used for the simultaneous separation of lignin from corn stover at 150 °C for 30 min, employing H_2SO_4 as a catalyst, achieving high yields for both lignin (75%) and hemicellulose (72%) [186]. H_2O/tetrahydrofuran (THF) assisted by Na_2CO_3 also showed 94.6% conversion of lignin from corncob residue, at 2 MPa of pressure at 140 °C for 1h, preventing the dissolution of cellulose [183]. Wyman et al. [184] compared the difference between two H_2SO_4 catalysed systems: H_2O/tetrahydrofuran (THF) and pure H_2O for maple wood degradation. The experiments were conducted at temperatures ranging 170-200°C with several reaction times (40-120 min). This comparison revealed that THF could significantly boost the efficiency of organosolv processes due to the good solubility of biomass decomposition products in THF, with more than 90% lignin recovery [184]. Furthermore, several organic acids were also tested in organosolv processes. Sun et al. [188] used an acetic acid-water system catalysed with HCl to extract lignin from bamboo. 95% of lignin and 48% of cellulose were recovered. The optimal delignification degree was achieved with 4 wt.% HCl in a 90 wt.% acetic acid-water solution using a batch reactor at 114°C for 2 h.

All these works published to date provide valuable information on the use of different organosolv systems for biomass fractionation. However, the work on analysing bamboo fractionation is very scarce [187, 196, 197] and, consequently, more research is needed for the valorisation of this biomass. In addition, these studies showed that the reaction conditions (especially the temperature, solvent

system and catalyst) exert a significant influence on biomass fractionation. Therefore, the large number of factors significantly influencing the process increases its intrinsic complexity. Moreover, some interactions between some of these factors could occur so that the effects of some variables may depend on others, resulting in different consequences for the process. These interactions have never been considered in the works addressing organosolv processes for biomass fractionation. Given this background, this work addresses the microwave-assisted fractionation of bamboo by means of an ethanol/water organosolv process catalysed by formic acid. In particular, the effects of the ethanol/water concentration (0-100 vol.%), catalyst (formic acid) amount (0-5 vol.%) and temperature (110-190 ºC) together with all the possible interactions between these variables on bamboo fractionation have been analysed in depth. Microwave heating represents a potentially faster, more efficient and selective process for the thermal treatment of biomass. As water and ethanol are highly effective in microwave energy absorption, the combination of an organosolv system together with microwave assisted heating offers an interesting new technology for the valorisation not only of bamboo but also of many other types of biomass. The fact that the combined effects of the operating variables and their interactions on an organosolv system has never been reported before demonstrate, together with the results provided by the in-depth study and the optimisation conducted, that this work represents a novel investigation in this field, which can help to develop a novel biorefinery concept based on bamboo fractionation, “the bamboo-refinery”.

3.3.3 Lignin as a potential nature UV blocker for broad spectrum sunscreen

Long time ultraviolet (UV) irradiation can cause skin problems and may even be carcinogenic. Sunscreen has been proven to be able to effectively protect skins [198]. Commercial sunscreens are broadly classified into two categories, i.e. physical sunscreen and chemical sunscreen respectively, according to their functional ingredients. Zinc oxide and titanium dioxide are the two major active ingredients in physical sunscreens, as they can reflect the sunlights [199]. In chemical sunscreens, a lot of different chemicals such as oxybenzone, avobenzone, octisalate, octocrylene can be found in the ingredient list. Those chemicals are rich in benzene rings, thus they can absorb UV lights efficiently. As introduced before, lignin is natually rich in aromatic rings, and it also contains proved UV absorbing functional groups such as phenolics, ketones, and other chromophores [200-202]. Zhu et al. have reported that alkali lignin can act as a nature derived additive to sunscreen to enhance the sun-proofing ability [203]. Organosolv process has shown the ability to produce high quality lignin, therefore, it worth to test if the microwave assisted bamboo organosolv lignin can be used in enhancing the sunproofing ability as an application [204].

3.4 EXPERIMENTAL FOR CHAPTER 3

3.4.1 Materials and chemicals for Chapter 3

Dried bamboo (*Phyllostachys heterocycle cv. pubescens*) was purchased from Anji County, Zhejiang Province, China. The raw bamboo was ground to 300 meshes. After grounding, the bamboo powder was washed by 50°C distilled water and then dried overnight at 105°C.

Nivea Sun Moisturising sun lotion with SPF 10, 30, 50 and Nivea light moisturising body lotion (SPF 0) were purchased from local Boots pharmacy shop, and used as received.

Microporous surgical tape was purchased from local Boots pharmacy shop as well.

3.4.2 Raw material characterisation for Chapter 3

This bamboo powder was characterised by means of proximate, ultimate and fibre (cellulose, hemicellulose and lignin) analyses, calorific value and ash content. Proximate analyses were performed according to standard methods (ISO-589-1981 for moisture, ISO-1171-1976 for ash and ISO-5623-1974 for volatiles). Elemental analysis, based on carbon, hydrogen and nitrogen content, was carried out using an Exeter Analytical (Warwick, UK) CE440 Elemental Analyser, calibrated against acetanilide with a S-benzyl-thiouronium chloride internal standard. Fibre characterisation was performed by using the chemical titration method described by Hu et al. [187] to determine the amount of cellulose, hemicellulose and lignin in the material (the detailed method is described in Appendix C). In addition, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to identify and quantify the amounts of metals.

3.4.3 Microwave experiments

The experiments were carried out in a CEM-Mars microwave system using a 70 mL scale PrepPlus® reactor copped with a fibre optic temperature sensor. For each experiment, 1.50 g bamboo powder along with 30 mL solvent (EtOH+H_2O) and catalyst (formic acid) mixture were loaded into the reactor. Before placing the reactor inside the microwave unit, the reaction mixture was pre-stirred at room temperature for 10 min. A ramping time (time to reach the reaction temperature) and a reaction time of 5 min and 15 min were respectively used for all the experiments. After reaction, the reactor cooled down to room temperature by CEM-Mars default programme. Then, the reactor was opened and its content, consisting of a mixture of liquid and solid, was transferred to a centrifuge tube. After that, the reactor was carefully rinsed with 10 mL of an ethanol/water (50 vol.%) solution for 3 times and transferred to the centrifuge tube to recover all the material. Centrifugation was used to separate the solid from the liquid. Then, the solid residue obtained after centrifugation was rinsed with the 50 vol.% ethanol-water solution until the solution remained clear, and dried overnight at 105°C. The liquid phase obtained was made up of a mixture of ethanol in water along with the hemicellulose and lignin fractions solubilised from bamboo during the microwave experiments. Finally, ethanol was removed from the liquid phase by means of a rotary evaporator, leading to lignin precipitation; thus allowing the separation of hemicellulose (water fraction) and lignin (solid fraction) by filtration. After this separation, part of the rich lignin solid was re-solubilised in ethanol (ethanol fraction) for further analysis. Figure 34 shows a schematic diagram of the fractionation process developed.

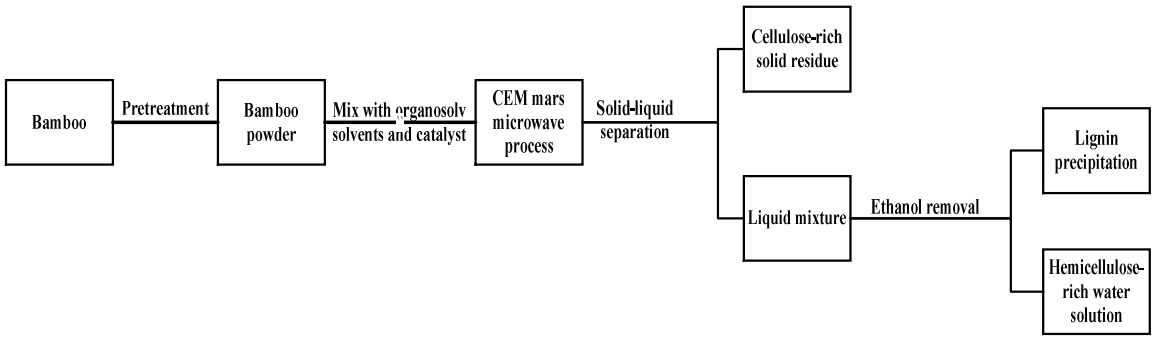

Figure 34: Fractionation process schematic diagram.

3.4.4 Response variables and analytical methods

Several response variables were used to analyse the effect of the operating conditions on the process. These include the overall bamboo conversion, the gas yields as well as the yields and the most important properties of the three fractions produced: i) a cellulose-rich solid fraction, ii) a hemicellulose rich water-soluble fraction and iii) a lignin rich solid fraction. Table 12 summarises the response variables and the analytical methods used for their calculation.

The solid residue produced after centrifugation was used to determine the conversion of cellulose, hemicellulose and lignin by using the chemical titration method described by Hu et al. [187]. In addition, this solid fraction was also analysed by X-ray Powder Diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD patterns were obtained from a Bruker AXS-D8 Advance diffractometer with a Kristalloflex 760 X-ray generator, which generates focused and monochromatized Kα X-rays from a Cu source. The samples were carefully milled into fine powders and placed evenly on a small round hole bevelled out of an aluminium sample holder. Scans were recorded across the range of 5-80 2θ over 10 minutes with a 40kV and 40mA current. Evaluation programme EVA and the Bruker CDS database were used to identify the phases present in the samples. SEM

pictures were taken with an INSPECT F, at an acceleration voltage of 20KV. Samples were coated with gold using a vacuum sputter-coater to improve the conductivity of the samples and the quality of the SEM pictures.

Table 12: Response variable and analytical methods used for their determination.

Response variables	**Analytical method**
Overall results	
Overall conversion (%) $= \left(1 - \frac{\text{mass of solid residue}}{\text{mass of bamboo}}\right) 100$	Mass difference
Hemicellulose rich fraction yield (%) $= \left(1 - \frac{\text{mass of gas (g)} + \text{mass of solid residue (g)}}{\text{mass of bamboo (g)}}\right) 100$	Mass difference
Cellulose rich fraction yield (%) $= \frac{\text{mass of solid residue (g)}}{\text{mass of bamboo (g)}} 100$	Mass difference
Lignin rich fraction yield (%) $= \frac{\text{mass of lignin (g)}}{\text{mass of bamboo (g)}} 100$	
Gas yield (%) $= \frac{\text{mass of gas (g)}}{\text{mass of bamboo (g)}} 100$	Mass difference
Cellulose rich fraction phase properties	
Composition (wt. %) $= \frac{\text{mass of structural component (g)}}{\text{mass of solid residue(g)}} 100$	Chemical titration
Lignin rich fraction phase properties	
Molecular weight (Da)	GPC (Gel permeation chromatography)

Hemicellulose rich fraction phase properties	
TOC	TC-IC measurement
$\text{Composition (C - wt.\%)} = \frac{\sum \text{mass of C of each compound (g)}}{\text{total mass of C in solution (g)}} 100$	HPLC (High performance liquid chromatography)

The water liquid phase was analysed by high-performance liquid chromatography (HPLC) and Total Organic Carbon (TOC), while the ethanol liquid phase containing ethanol-soluble lignin was characterised by GPC. HPLC analyses were conducted with an Agilent Technologies 1200 series HPLC system employing a XDB-C18 column and a UV detector. A Waters GPC device equipped with a 2414 refractive index detector was used with Waters Strygel columns HT4 and HT3 in series. Empower III GPC software was used for running the GPC instrument and for calculations. Both the columns and the RI detector were maintained at 45°C for analysis. TOC analyses were conducted in a Vario TOC Cube Analyser.

3.4.5 Preparation of lignin sunscreen samples and determination of sunscreen effect

All the lignin-based sunscreen creams were prepared by simple magnetic stirring. 0.3 g of lignin was loaded into 3 g of Nivea cream with different SPF value respectively. And stirred at 1000 rpm for 24 hours. The mixing process was performed under room temperature in a dark cupboard. The Boots microporous surgical tape was cut into 22 × 50 mm rectangle pieces and stick the tape on a glass cover slip (22 × 50 mm). The glass cover slip covered by microporous surgical tape

was placed on an analytical balance, 22 mg of cream/lignin-cream mixture was carefully dotted on the surface of the microporous surgical tape by a 1 ml fine needle syringe. The cream/lignin-cream mixture was distributed over the entire surface evenly by robbing the surface with a cot coated finger. The same process was repeated for every Nivea cream and lignin-cream mixture. The sample was placed in dark for 30 min for drying before UV measurement.

The UV transmittance of the sunscreens and lignin sunscreens were measured by JASCO V-550 UV/VIS Spectrophotometer with an integrating sphere (JASCO, Japan). Three spots were scanned for each sample. In each scan, transmittance measurement was collected at every 1 nm in the wavelength range from UVB (280 – 320 nm) to UVA (320 – 400 nm).

3.4.6 Experimental design and data analysis

The influence of reaction temperature (110-190°C), ethanol concentration in water (0-100 vol.%) and the amount of formic acid, used as a homogeneous catalyst, (0-5 vol.%) on bamboo fractionation was experimentally investigated. The experiments were planned according to a 2 level 3-factor Box-Wilson Central Composite Face Centred (CCF, α: ±1) design. The results were analysed with an analysis of variance (ANOVA) with 95% confidence. The ANOVA analysis helped for the selection of the operating variables and interactions that significantly influence the response variables under consideration. In addition, the cause-effect Pareto principle was used to calculate the relative importance of the operating variables in the response variables. In these analyses, the lower and upper limits of all the operating variables (temperature, EtOH/H_2O and catalyst amount) were normalised from -1 to 1 (code variables). This codification permits all operating variables (factors) to vary within the same interval and helps to investigate their influence in comparable terms.

3.5 RESULTS AND DISCUSSION

3.5.1 Bamboo characterisation

Table 13 lists the characterisation results of bamboo. These include the proximate, ultimate and fibre analyses, the ash content and higher heating value (HHV). These results are fairly similar to those reported in the literature [205-207]. The presence of inorganics in bamboo is accounted for by the presence of powder derived from soil. Ca, Mg, K, Na, P and Si are the major inorganics detected. In addition, traces of other inorganic components, such as Fe, Al, S and Mn were also found in the feedstock.

Table 13: Proximate, fibre, elemental and calorific analyses of the bamboo used in this work.

Proximate analysis (wt.%)	
Moisture	3.46
Ash	8.15
Volatiles	63.52
Fixed carbon	20.31
Fibre analysis (wt.%)	
Cellulose	45.01±1.41
Hemicellulose	25.98±0.66
Lignin	20.80±0.17
Ash	8.15%
Elemental analysis (wt.%)	
C	47.58±0.34
H	5.83±0.03
N	0.48±0.04
O*	37.96±0.33
HHV (MJ/kg)	19.61±0.13
Ash composition (ppm)	

Ca	500
Mg	257.4
K	292
Na	170.41
P	108
Si	107

*Oxygen was calculated by difference

Table 14: Experimental conditions: temperature (ºC), solvent system (EtOH/H2O, vol. %) and formic acid (vol. %) and results obtained in the experiments

Run	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9-12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
T (ºC)	110	190	110	190	110	190	110	190	150	110	190	150	150	150	150	190
EtOH/EtOH+H_2O (vol.%)	0	0	100	100	0	0	100	100	50	50	50	0	100	50	50	50
Formic acid (vol. %)	0	0	0	0	5	5	5	5	2.5	2.5	2.5	2.5	2.5	0	5	5
Overall results																
Overall conversion (%)	6.55	34.74	10.27	12.62	14.12	48.75	5.59	16.45	20.27±1.71	13.43	46.91	29.79	10.80	20.63	19.04	49.00
Hemicellulose fraction yield (%)	4.17	23.22	6.77	8.12	10.98	32.33	2.33	10.94	12.35±1.46	9.04	24.04	23.60	7.44	12.22	11.73	25.82
Cellulose fraction yield (%)	93.45	65.26	89.73	87.38	85.88	51.25	94.41	83.55	79.73±1.71	86.57	53.09	70.21	89.20	79.37	80.96	51.00
Lignin fraction yield (%)	2.39	11.52	3.50	4.51	3.14	16.42	3.26	5.50	7.93±0.60	4.39	22.87	6.19	3.35	8.42	7.31	23.17
Gas yield (%)	1.36	3.23	2.94	2.31	4.85	8.67	3.76	2.39	2.79±0.64	2.45	2.47	2.25	2.58	1.47	2.44	3.74
Hemicellulose rich fraction fibre analysis																
Cellulose (wt.%)	43.94	57.62	49.33	51.85	55.82	61.92	49.33	46.78	52.86±2.87	49.65	61.55	49.32	56.79	54.61	45.79	83.00
Hemicellulose (wt.%)	14.88	4.22	19.57	15.76	17.82	0.00	18.95	19.10	14.09±0.79	19.85	2.46	7.20	20.86	15.10	12.99	1.99
Lignin (wt.%)	25.15	24.22	24.98	24.53	34.23	19.16	23.99	24.49	23.65±1.34	26.95	30.53	25.29	22.21	23.10	25.82	12.52
Lignin rich phase																

Mw (Da)	600	1528	3177	2758	2039	1053	3133	2540	2142±261	2262	1614	1567	2768	3060	2201	2323
Hemicellulose rich phase composition																
TOC (ppm)	0	353.05	174.37	34.31	206.44	157.76	89.69	56.06	148.75±90.27	34.52	172.94	126.11	56.58	177.44	93.28	397.27
Sugars (C- wt.%)	0	2.66	0	1.19	0.53	42.68	0.66	1.66	2.33±1.75	3.86	15.98	32.01	1.95	1.42	1.52	11.52
Acids (C- wt.%)	0	6.43	0	19.56	95.45	53.94	99.34	37.98	81.43±11.07	85.84	27.17	26.59	98.03	32.86	82.99	60.65
Oligomers (C- wt.%)	100.00	90.88	100.00	79.19	0	0	0	60.36	5.50±4.20	0	56.19	41.39	0.00	65.72	0	27.71

Table 15: Relative influence of the operating conditions according to the ANOVA analysis.

Variable	R^2	I.Term	A (T)	B (EtOH%)	C (formic acid)	AB	AC	BC	ABC	A^2	B^2	C^2	A^2B	A^2C	AB^2	AC^2	A^2B^2
Overall results																	
Overall conversion (%)	0.99	20.17	16.21	-7.82	n.s	-6.2	1.74	-2.8	n.s.	9.48	n.s.	n.s.	n.s.	2.46	-6.71	n.s.	-11.01
			(28)	(17)		(12)	(7)	(5)		(3)				(8)	(8)		(11)
Hemicellulose fraction																	
yield (%)	0.99	12.22	6.52	-8.08	n.s	-3.8	1.18	-2.19	n.s	4.25	3.3	n.s	2.76	1.77	n.s	n.s	-7.41
			(28)	(22)		(13)	(6)	(7)		(1)	(3)		(4)	(7)			(8)
Cellulose fraction yield																	
(%)	0.99	79.83	-16.21	9.5	n.s	6.2	-1.74	2.8	n.s	-9.47	n.s	n.s	-2.09	-2.46	6.71	n.s	11.01
			(28)	(17)		(12)	(6)	(5)		(3)			(2)	(8)	(8)		(11)
Lignin fraction yield (%)	0.99	7.91	8.98	-1.95	n.s	-2.39	0.61	-0.61	n.s	5.46	-3.14	n.s	n.s	0.73	-5.77	n.s	-3.95
			(26)	(9)		(10)	(7)	(3)		(4)	(18)			(5)	(13)		(5)
Gas yield (%)	0.92	2.45	n.s	n.s	n.s	-0.96	n.s	-1	n.s	n.s	n.s	n.s	-0.84	1.19	n.s	0.42	1.24
						(17)		(18)					(18)	(23)		(7)	(18)
Solid residue fractionation composition																	
Cellulose (wt.%)	0.92	52.54	5.95	n.s	-4.41	-2.48	n.s	-2.66	n.s	n.s	n.s	n.s	-2.75	5.8	-26.6	23.12	n.s
			(20)		(9)	(7)		(8)					(9)	(10)	(17)	(20)	

Hemicellulose (wt.%)	0.99	14.06	-8.75 (26)	6.83 (22)	-1.05 (3)	3.1 (12)	-0.41 (4)	0.5 (2)	1.39 (6)	-2.96 (4)	n.s	n.s	-2.27 (4)	1.22 (1)	4.73 (10)	n.s	2.69 (6)
Lignin (wt.%)	0.95	23.88	1.79 (16)	-0.79 (5)	n.s	2.01 (12)	-1.65 (17)	n.s	1.89 (12)	4.86 (5)	n.s	n.s	n.s	n.s	12.58 (0)	-16.36 (22)	-3.65 (10)
Lignin phase																	
MW (Da)	0.92	2097.5	-169.77 (8)	758.9 (40)	-429.5 (1)	n.s	-258.46 (10)	n.s	217.5 (11)	n.s	n.s	543.15 (5)	n.s	519.79 (13)	n.s	n.s	-537.15 (13)
Water phase properties																	
TOC (ppm)	0.92	125.36	69.21 (15)	-43.23 (13)	n.s	-59.76 (16)	-36.91 (3)	n.s	63.52 (18)	n.s	n.s	n.s	n.s	n.s	-292.49 (17)	239.61 (17)	n.s
Sugars (C- wt. %)	0.93	13.5	n.s	27.83 (5)	n.s	-22.44 (18)	n.s	n.s	-22.15 (18)	n.s	57.79 (12)	n.s	-28.18 (10)	24.18 (21)	n.s	n.s	-44.9 (15)
Acids (C- wt.%)	0.96	76.79	-29.33 (10)	35.72 (6)	31.54 (26)	n.s	-15.54 (12)	n.s	n.s	-14.52 (15)	-10.97 (7)	-13.09 (6)	-35.59 (11)	n.s	n.s	20.29 (7)	n.s
Oligomers (C- wt.%)	0.99	6.01	28.1 (5)	-20.7 (1)	-37.75 (26)	6.08 (4)	11.03 (8)	9.01 (6)	9.01 (6)	21.07 (15)	14.69 (6)	25.83 (8)	26.78 (7)	n.s	n.s	-24.55 (7)	-13.8 (2)

n.s: Non significant with 95% confidence

Response = Indep. + Coefficient A·A + Coefficient B·B + Coefficient C·C + Coefficient AB·AB + Coefficient AC·AC Coefficient BC·BC Coefficient ABC·ABC + Coefficient $A^2 \cdot A^2$ + Coefficient $B^2 \cdot B^2$ + Coefficient $C^2 \cdot C^2$ + Coefficient $A^2B \cdot A^2B$ + Coefficient $A^2C \cdot A^2C$ + Coefficient $AB^2 \cdot AB^2$ + Coefficient $AC^2 \cdot AC^2$ + Coefficient $A^2B^2 \cdot A^2B^2$

Numbers in brackets indicate the percentage Pareto influence of each factor on the response variable. Pareto values represent the percentage of the orthogonal estimated total value.

3.5.2 Effects of operating conditions on the overall conversion and products distribution

Table 14 summarises the operating conditions for the experiments and the experimental results. The overall bamboo conversion and the yields to gas, lignin-rich solid fraction, hemicellulose rich water fraction and cellulose rich solid fraction vary as follows: 1-9%, 6-49%, 2-23%, 2-32% and 51-94%, respectively. The relative influence of the operating variables on the global bamboo conversion and the yields of the three main fractions produced according to the ANOVA analysis, and the cause-effect Pareto principle is shown in Table 15.

According to the cause-effect Pareto analysis, the temperature (with more than 26% of influence) is the operating variable exerting the greatest influence on the overall bamboo conversion and the yields to lignin, hemicellulose and cellulose rich solid fractions. In addition, the concentration of ethanol and the interactions (both linear and quadratic) between the temperature and the concentration of ethanol also exert a significant influence on these response variables with more than 12% influence in all cases. The concentration of formic acid (catalyst) alone does not have a significant influence on these response variables. However, its interaction with the temperature is significant, thus suggesting a synergistic effect between these two variables; i.e. a certain temperature is needed for the acid to catalyse the process significantly. The gas yield is greatly influenced by the interaction between the temperature and the concentration of ethanol in water.

As regards the influence (positive or negative) of the operating variables on the process, the coefficients in the models indicate that an increase in the temperature leads to an increase in the overall conversion, the hemicellulose rich fraction and lignin rich fraction yields (positive terms), and a decrease in the cellulose rich solid fraction yield (negative term). The concentration of ethanol in water exerts the opposite effect; i.e. an increase in the proportion of ethanol results in a decrease in the overall bamboo conversion and the hemicellulose rich fraction and lignin rich fraction yields (negative terms) along with an increase in the cellulose rich solid fraction (positive terms). Moreover, as commented above, significant interactions between variables also take place, demonstrating that the other operating variables influence the effect that each variable has on the process. To gain a better understanding of the process, Figure 35 displays the effect of the operating variables and the most important interactions detected with the ANOVA analysis. Specifically, Figure 35 a and b illustrates the effect of the ethanol concentration and the temperature on the overall bamboo conversion in the absence of catalyst (formic acid = 0 vol.%) and for the highest amount of catalyst used in this work (formic acid = 5 vol.%), respectively. These effects are also shown for the lignin rich fraction, hemicellulose rich fraction and cellulose rich fraction yields in Figures 35 c-d, e-f and g-h, respectively.

As regard the effects of the temperature, Figure 35 shows that regardless of the other operating conditions, the temperature exerts a positive effect on bamboo decomposition. Specifically, an increase in temperature from 110 to 190 ºC substantially increases the overall bamboo conversion as well as the yields of the lignin and hemicellulose fractions; which consequently results in a decrease in the cellulose fraction yield. The temperature

positively enhances the kinetics of the process and greater microwave power is also needed to achieve higher temperatures, thus promoting the break of the intramolecular bonds between cellulose, hemicellulose and lignin in bamboo. Kassaye et al. [205] reported a similar trend during the hydrolysis of bamboo between 90 and 150 ºC with NaOH for 30 min.

The effect of the concentration of ethanol in water (solvent system) depends on the temperature due to the significant interaction detected between both variables, with two different developments occurring. At low temperature (110 ºC) the solvent system does not exert a very important influence on the process, and similar conversions and yields to products are obtained regardless of the solvent composition, either using the pure solvents (ethanol and/or water) or any binary mixture. This suggests that a certain temperature is needed to both break the intramolecular bonds between the bamboo structural components and solubilise the released fractions into the solvent system. This is a consequence of the kinetics of the process and is in good agreement with the cause-effect Pareto results, which indicated that the temperature was the operating variable exerting the greatest influence on the overall conversion and the yields to different fractions. High temperatures are needed to achieve good conversion during the very short reaction (15 min) time employed in this work.

Conversely, as the temperature increases, the solvent system has a more important influence on the process, and an interaction between ethanol and water takes place. In particular, a synergetic interaction between EtOH and H_2O occurs for the overall bamboo

conversion and the yields to lignin and cellulose fractions. In particular, higher values are obtained for the bamboo conversion and the yield of lignin fraction and lower values for the yield of cellulose fraction with an EtOH/H_2O mixture than using the pure solvents (EtOH or H_2O alone), with a maximum occurring with a concentration of EtOH of around 40-50 vol.%. This maximum is in good agreement with other results reported in the literature [208-212] where maxima for lignin conversion occurred employing a concentration of 40-60 vol.% of EtOH in water.

This interaction is more obvious for the lignin yield than for the other variables, and it does not take place for the hemicellulose fraction yield, thus suggesting that the solvent system exerts the greatest influence on lignin fractionation. For lignin extraction, a nucleophilic solvent such as water is needed for extracting lignin from the biomass structure along with another solvent to dissolve the extracted lignin [192]. Water alone can extract lignin, however, the solubilisation of this lignin by water is the limiting step. Conversely, ethanol is not appropriate for lignin extraction, but it promotes lignin solubilisation. Therefore, the presence of both solvents in the system promotes both lignin extraction and solubilisation; which, therefore, significantly increases the lignin yield. This synergetic interaction does not take place for the hemicellulose fraction yield, for which the highest yield is produced with pure water; the addition of ethanol into the system progressively decreases the yield of this fraction. In addition, this effect is too weak for the rich cellulose solid fraction. These developments are a consequence of the different polarities of these two fractions compared to lignin as well as due to the lesser spread of hydrolysis reactions to extract hemicellulose in ethanol than in water [213].

The effect of the catalyst concentration on the overall bamboo conversion and the yields to the lignin, hemicellulose and cellulose rich fractions can be observed comparing a,c,e, and g with b, d,f and h in Figure 35 respectively. This comparison reveals that the effect of the catalyst for these response variables is relatively weak as predicted by the Pareto Analysis. In addition, the effect depends on the temperature. At low temperature (110ºC) the effect of the addition of up to 5 vol.% of formic acid in the process is almost negligible. However, at 190 ºC the catalyst exerts a more pronounced effect on bamboo decomposition as the kinetics of the process is enhanced. In addition, at this temperature, the specific effect of the catalyst depends on the solvent system. While an increase in the amount of catalyst promotes bamboo decomposition (increases bamboo conversion/decreases the cellulose solid yield and increases the yields to lignin and hemicellulose rich fractions) with pure water, the addition of ethanol progressively decreases the catalytic effect of formic acid in the process due to the lower solubilisation of formic acid protons in ethanol than in water [213].

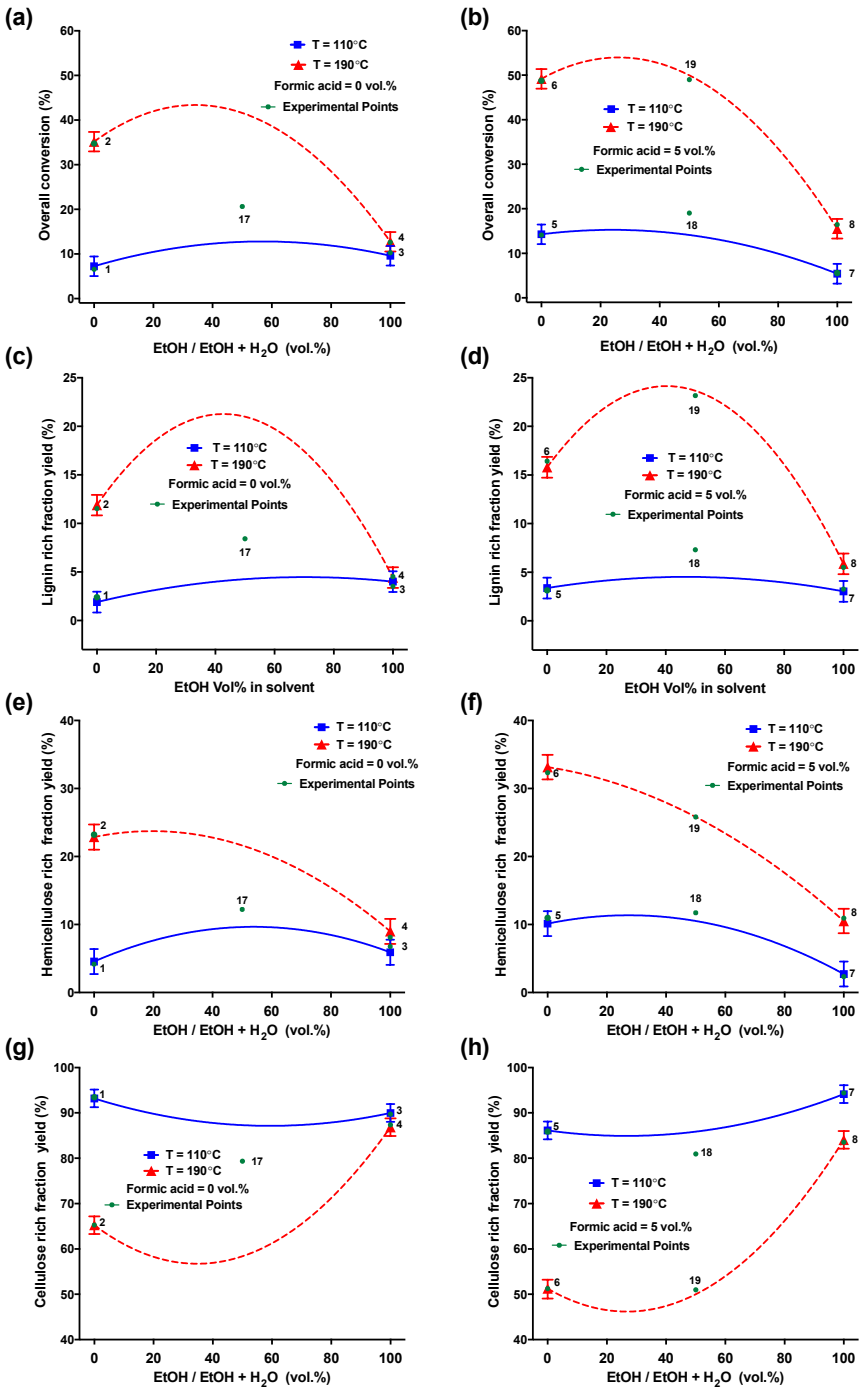

Figure 35: Interaction plots between the temperature and the solvent system (EtOH/H2O) without/with catalyst for the overall bamboo conversion (a/b), lignin rich solid fraction yield (c/d), hemicellulose rich liquid fraction yield (e/f), and cellulose rich solid

3.5.3 Effects of operating conditions on the properties of each fraction

This section examines the effects of the operating conditions on several of the most important properties of the three products produced during the fractionation of bamboo: i) the cellulose-rich spent solid fraction, ii) the hemicellulose rich water sample fraction and iii) the lignin rich fraction.

3.5.3.1 Cellulose-rich solid fraction

This cellulose-rich solid fraction consists of the solid residue obtained by filtration after the microwave treatment of bamboo. The characterisation of this solid by chemical titration revealed that this fraction contains cellulose and, in less proportion, unreacted hemicellulose and lignin with varying compositions depending on the operating conditions. The amounts of cellulose, hemicellulose and lignin in the spent solid vary by: 44-83 wt.%, 0-21 wt.% and 12-34 wt.%. The effect of the operating conditions on the composition of this fraction according to the ANOVA analysis, and the cause-effect Pareto principle is shown in Table 15. The temperature and its interaction with the catalyst amount and in lesser extent with the solvent system are the factors exerting the greatest influence on the proportions of cellulose and lignin. The temperature, the solvent system and the interaction between these two variables primarily influence the proportion of hemicellulose. The effects of the operating conditions and interactions between them on the relative amounts of cellulose, hemicellulose and lignin are plotted in Figure 36. In particular, a, b and c in Figure 36 shows the effects of the solvent system and the temperature in the absence of catalyst. Figure 36 d, e and f show these effects when using the highest concentration of catalyst (5 vol.%) employed in this work.

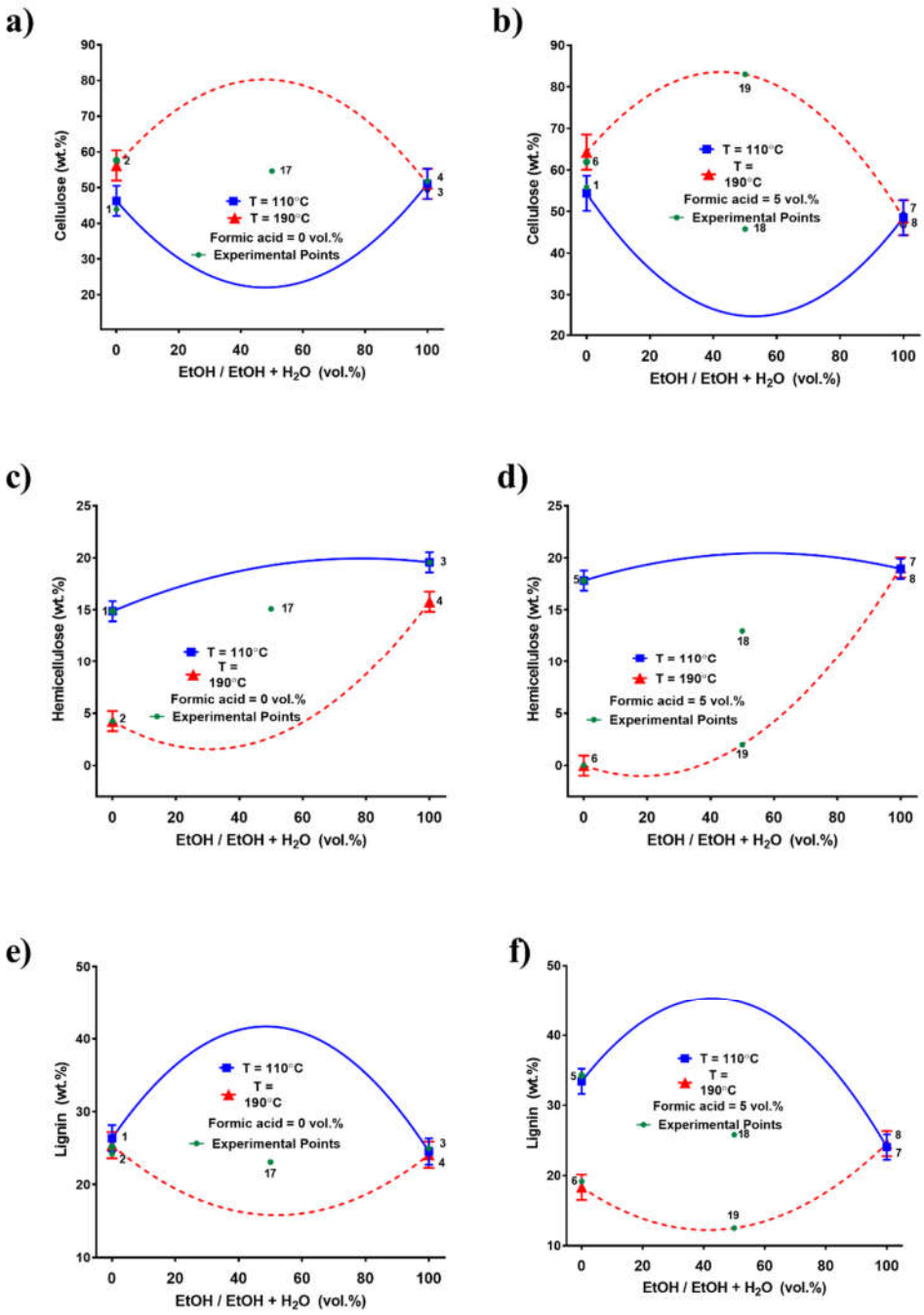

Figure 36: Interaction plots between the temperature and the solvent system (EtOH/H2O) without/with catalyst for the relative amounts of cellulose (a/b), hemicellulose (c/d) and lignin (e/f) of the cellulose rich solid fraction. Bars are LSD intervals with 95% confidence.

With respect to the effects of the temperature on the composition of the cellulose rich fraction, Figure 36 shows how regardless of amount of catalyst employed (0-5 vol.% formic acid), an increase in the temperature between 110 and 190 ºC results in a decrease in the proportions of hemicellulose and lignin, and consequently, the proportion of cellulose increases. An increase in the temperature helps to solubilise the hemicellulose and lignin fractions of bamboo into the solvent system, and therefore a cellulose-rich solid is obtained due to the positive kinetic effect of the temperature in the process. A solid with a high proportion of hemicellulose (80-85%) can be obtained at 190 ºC employing a concentration of EtOH of around 40-50 vol.%. This is in good agreement with other works where the EtOH/H_2O solvent system was used for the fractionation of biomass [208-212].

In addition, an interaction between the temperature and the solvent system was detected in the ANOVA analysis and can be observed from the results plotted in Figure 36. This indicates that the effect of the temperature depends on the solvent system and vice versa. The temperature has a significant influence on the process for the majority of the binary mixtures considered (between 15 and 85 wt.% of ethanol in water). However, for the pure solvents or high concentrated in one compound (>85 wt.%) binary mixtures, the effect of the temperature decreases dramatically, being insignificant in some cases. This development might be a consequence of the positive influence of the temperature on the solvent system in this work.

At 190 ºC, the positive kinetic effect of the temperature can mask the effect on the solvent system on lignin solubilisation, resulting in a cellulose solid fraction with similar lignin

content regardless of the solvent system. Conversely, the effect of the solvent can be observed at low temperature. Pure water helps lignin depolymerisation [192], while ethanol can react with α-hydroxyl groups in bamboo to increase the solubility of lignin, preventing its condensation; thus decreasing the lignin content of this fraction at 110 ºC [192]. For these reactions to take place at low temperature, high biomass/ethanol and biomass/water ratios might be needed, therefore pure solvents are required, and the synergetic effect between both solvents does not take place a low temperature. The opposite effect takes places for the relative amount of hemicellulose in the solvent system; i.e. the proportion of hemicellulose is not strongly influenced by the solvent system at low temperature, and this fraction has a high proportion of hemicellulose due to the low solubilisation of this structural component at low temperature. Conversely, the solvent system exerts a significant influence on the relative amount of hemicellulose at high temperature (190ºC). Using pure water the proportion of hemicellulose in the solid is very low, and the addition up to a 40 vol.% of ethanol in the system does not influence the relative amount of hemicellulose in the solid. However, a further increase in the proportion of ethanol from 40 to 100 vol.% results in a sharp increase in the relative amount of hemicellulose in the spent solid due to the lesser spread of hydrolysis reactions to extract hemicellulose in ethanol than in water [213]. The variations observed for the relative amount of cellulose in this fraction are related to the variations observed for hemicellulose and lignin, as this fraction is not very reactive under the operating conditions tested in this work.

The catalyst exerts a weak effect on the proportions of cellulose, hemicellulose and lignin of this fraction, with two different effects occurring depending on the temperature. At low

temperature an increase in the amount of formic acid between 0 and 5 vol.% leads to a decrease in the proportion of cellulose along with an increase in the relative amount of hemicellulose and lignin, the opposite is observed at high temperature (190 ºC); i.e. the proportion cellulose increases and the relative amounts of hemicellulose and lignin decrease.

3.5.3.2 Lignin-rich solid fraction

This rich lignin fraction consists of the solid residue produced after removing the ethanol from the liquid collected after the microwave experiments. The lignin content of this solid fraction was greater than 95 wt.%, which is in good agreement with other works reported in the literature that regard this solid as high purity organosolv lignin. This highlights the good controllability and selectivity of this microwave-assisted organosolv process for the fractionation of bamboo. The molecular weigh of this fraction, determined by GPC, shifts between 600 and 3177 Da. The effects of the operating conditions on the molecular weight of the organosolv lignin produced according to the ANOVA analysis, and the cause-effect Pareto principle is shown in Table 15. This analysis shows that the solvent system (ethanol concentration in water) is the factor exerting the greatest importance on the molecular weigh of this fraction, the temperature and the catalyst amount having a lower influence. Figure 37 a and b show the effect of the solvent system on the molecular weight of the organosolv lignin produced at low and high (110 and 190 ºC) temperatures for two catalyst loadings: 0 vol.% and 5 vol.%, respectively. Regardless of the temperature and the catalyst loading, this fraction has the lower molecular weight when only water is used in the process. The addition of up to 45-50 vol.% of ethanol in the solvent mixture increases the molecular weight of this fraction, while a further increase of up to 100 vol.% does not modify the

molecular of the lignin produced. The presence of water in the solvent system helps to depolymerise lignin, thus decreasing the molecular weight of the lignin produced [191].

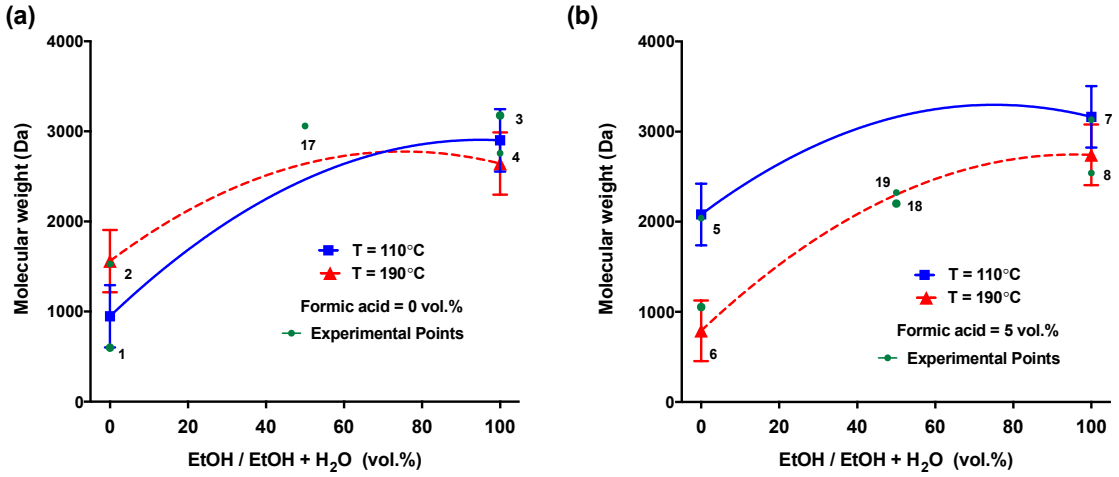

Figure 37: Interaction plots between the temperature and the solvent system (EtOH/H2O) without/with catalyst (a/b) for the molecular weight of the lignin produced. Bars are LSD intervals with 95% confidence.

The effect of the temperature depends on the catalyst amount. On the one hand, in the absence of a catalyst, the temperature does not exert a significant influence regardless of the solvent system. On the other, when the highest amount of catalyst is used, the effect of the temperature depends on the solvent system with two developments observed. In particular, an increase in the temperature decreases the molecular weight of lignin when pure water is used. The addition of ethanol progressively reduces the effect of the temperature and as a consequence, the effect of this variable stops exerting a significant influence on the molecular weight of the organosolv lignin produced for concentrations of ethanol higher than 75 vol.% due to the lower effectiveness of ethanol than water in lignin depolymerisation [191].

3.5.3.3 Hemicellulose-rich liquid fraction

This fraction comprises water-soluble hemicellulose decomposition products. It is made up of a mixture of oligomers, sugars (cellobiose, glucose and xylose), carboxylic acids (acetic acid), ketones (γ-valerolactone, GVL) and furans (furfural and 5-hydroxymethylfurfural, HMF). The relative amounts (in C basis) of these families of compounds vary by 0-100 wt.%, 0-100 wt.%, 0-100 wt.%, 0-13 wt.% and 0-4 wt.%, respectively. Table 15 lists the effects of the operating conditions on the composition of this fraction according to the ANOVA analysis and the cause-effect Pareto principle. This analysis indicates that the operating conditions do not exert a significant influence on the relative amounts of ketones and furans of this fraction, probably due to their low concentration in the liquid phase under the operating conditions used in this work. The statistical analysis shows that the interaction between the temperature and the solvent system is the factor with the highest influence on the proportion of sugars, while the amount of catalyst is the operating variable exerting the highest impact on the relative amounts of carboxylic acids and oligomers. In addition, significant interactions between the operating variables also take place.

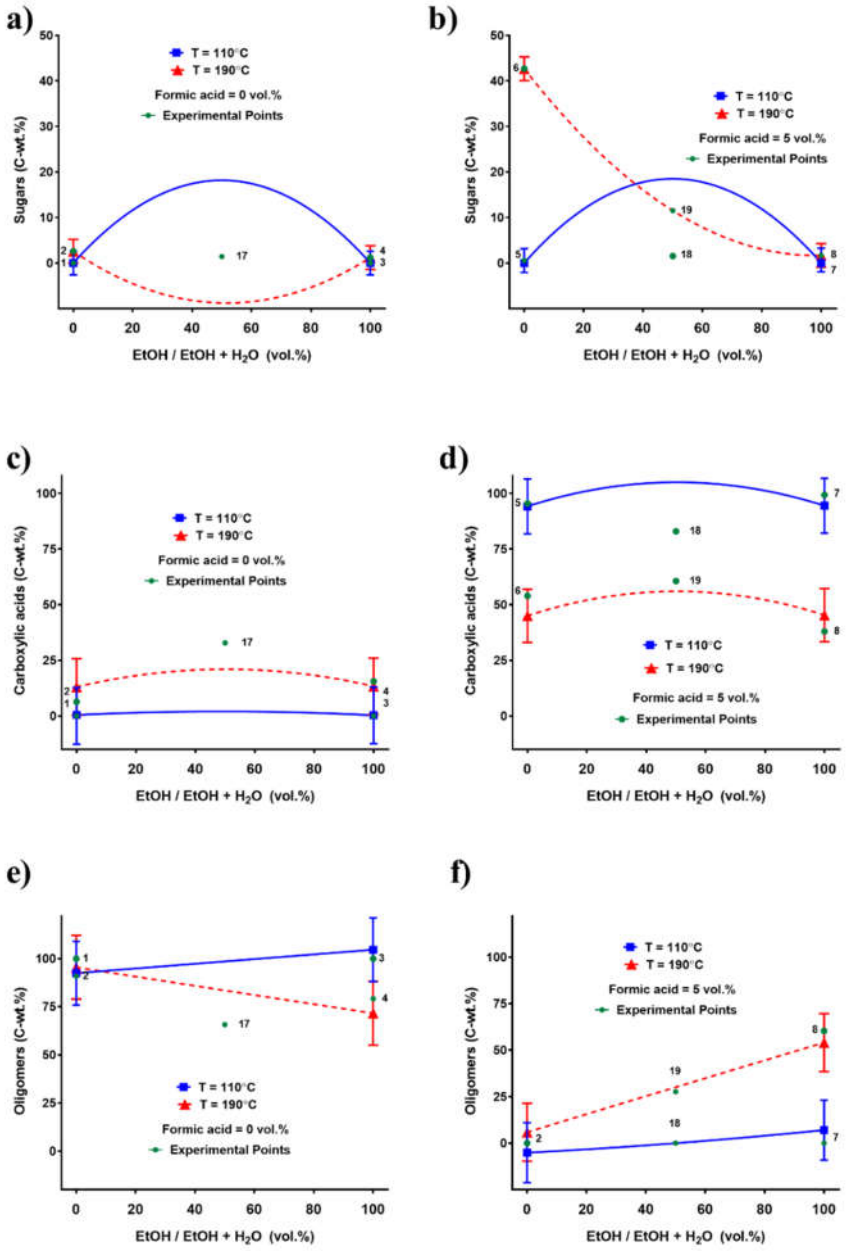

Figure 38: Interaction plots between the temperature and the solvent system (EtOH/H2O) without/with catalyst for the relative amounts of sugars (a/d), carboxylic acids (b/e) and oligomers (c/f) present in the water-soluble hemicellulose rich fraction. Bars are LSD intervals with 95% confidence.

The effect of the operating conditions and the most important interactions for the proportions of sugars, carboxylic acids and oligomers are shown in Figure 38. In the absence of a catalyst, this hemicellulose rich water fraction is primarily made up of oligomers, the proportions of sugars and carboxylic acids being quite low regardless of the solvent system. Conversely, the addition of a catalyst (formic acid) decreases the proportion of oligomers and increases the concentration of sugars, and carboxylic acids in this fraction. At low temperature (110 ºC) carboxylic acids are the most abundant compounds of this fraction, while an increase in the temperature increases the relative amounts of sugars and oligomers and decreases the proportion of carboxylic acids in the liquid due to greater conversion of hemicellulose and lignin. At 190 ºC the proportion of carboxylic acids is not influenced by the solvent system, while this operating variable exerts a significant influence on the relative amounts of sugars and oligomers. With pure water, this fraction has a high concentration of sugars, and a negligible quantity of oligomers is observed. The increase of the proportion of ethanol in the solvent system decreases the proportion of sugars and increases the proportion of oligomers. The presence of water in the solvent system promotes hydrolysis reactions, thus decreasing the proportion of oligomers and, therefore, increasing the amount of sugars [192].

3.5.4 Optimisation of the fractionation process

Optimum conditions were sought for the selective fractionation of bamboo making use of the experimental models developed. The predicted R^2 of all the models are greater than 0.90, allowing their use for prediction purposes within the range of study. The optimisation process comprises the minimisation of the cellulose conversion (maximisation of the cellulose solid rich fraction and proportion of cellulose of this fraction) and the

maximisation of the yields of hemicellulose rich and lignin rich fractions. To meet this objective, a solution that strikes a compromise between the optimum values for all the response variables was sought. To do so, a relative importance (from 1 to 5) was given to each of the objectives in order to come up with a solution that satisfies all the criteria. Table 15 lists the relative importance assigned to each variable as well as the criteria used in the whole optimisation.

Taking these conditions into account, the optimisation predicts an optimum at 190 ºC using a solvent system consisting of 45% EtOH/50% H_2O (vol/vol) with a concentration of formic acid of 5 vol.%. Under these conditions, it is possible to selectively fractionate bamboo into cellulose, hemicellulose and lignin. The cellulose rich fraction contains 84 wt.% of cellulose and 12 wt.% of lignin. The yield to organosolv lignin is very high (24%), which corresponds to a recovery of 90 wt.% of the lignin present in the original bamboo. In addition, hemicellulose is completely removed from the original feedstock, and a water solution consisting of a mixture of oligomers, sugars and carboxylic acids can be produced. This optimum was checked experimentally (Table 16) and non-statistically significant differences were found between the theoretical prediction and the experimental results with 95% confidence.

Table 16: Theoretical optimisation: operating conditions and response variables: objectives, the interval of variations, relative importance, theoretical and experimental optimum values.

Variables	Objective	Interval of variation	Relative importance (1-5)	Optimum Theoretical	Optimum Experimental
Temperature (ºC)	none	110-190		190	
EtOH/EtOH+H_2O (vol.%)	none	0 - 100		45	
HCOOH (vol.%)	none	0 - 5		5	
Overall Conversion (%)	maximise	0-100	3	52	51.23
Cellulose rich faction					
Yield (%)	maximise	0-100	3	49	50.46
Cellulose content (wt.%)	maximise	0-100	5	84	84.87
Hemicellulose content (%)	minimise	0-100	5	1	1.85
Lignin Content (%)	minimise	0-100	5	12	11.55
Lignin rich fraction					
Yield (%)	maximise	0-100	3	24	23.87
Molecular weight (DA)	none			2203	2201
Hemicellulose rich fraction					
Yield (%)	maximise	0-100	3	27	26.82
Oligomers (C-wt.%)	none	0-100		27	27.80
Sugars (C-wt.%)	none	0-100		56	60.11
Carboxylic acids (C-wt.%)	none	0-100		14	12.65

To gain a better insight into this fractionation process, the original bamboo and the spent solid produced at the optimum condition were characterised by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD), and a comparison was established

between both materials. The SEM images (Figure 39) show how after the microwave-assisted organosolv treatment the original micro-fibrous structure of bamboo disappears and the solid residue surface becomes significantly rougher. In addition, some small spheroidal particles appeared on the cellulose fibrillar structure after the treatment (under 1500 magnification), which was possibly caused by lignin precipitation onto the fibres [214, 215]. These differences suggest that most of the lignin and hemicellulose are removed during the organosolv process. A small quantity of lignin still remains on the surface of the cellulose rich fraction due to the lignin condensation. These developments are in a good agreement with the experimental results listed in Table 16.

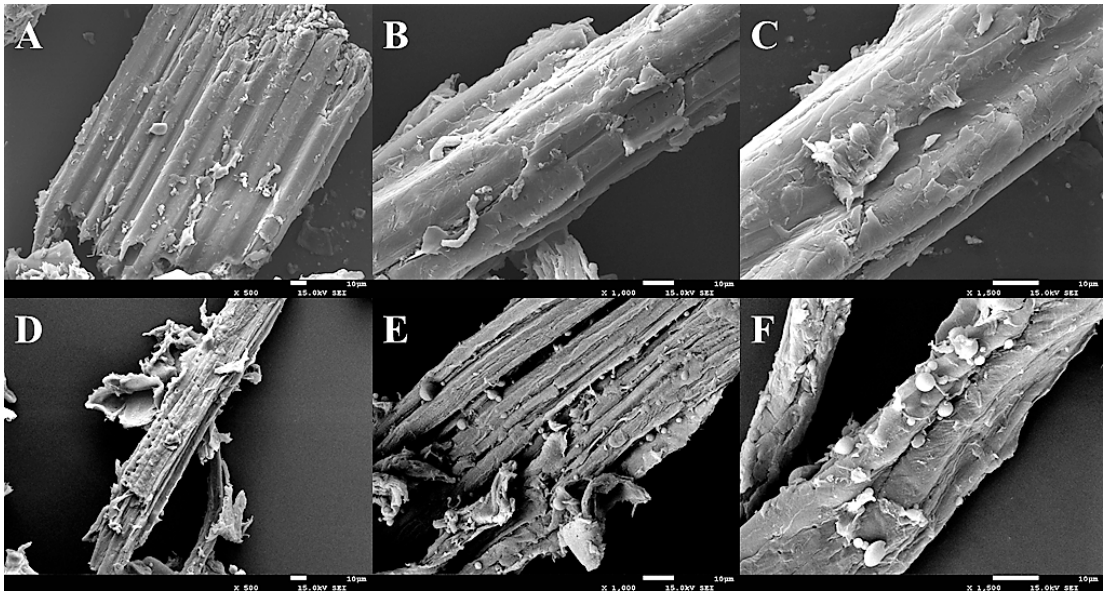

Figure 39: SEM images of bamboo powder (A: ×500, B: ×1000, C: ×1500) and optimum experimental run solid residue (D: ×500, E: ×1000, F: ×1500).

XRD was used to evaluate the effectiveness of the optimised microwave assisted organosolv process by comparing the degree of crystallinity (DoC) of both materials

(before and after the treatment) [216, 217]. Figure 40 shows the XRD patterns for the original material and the spent solid (high purity cellulose fraction) produced after the microwave treatment. The comparison of both spectra does not show great differences between both solids, which is in good agreement with the experimental results, as only crystal cellulose can be detected by XRD. In addition, the crystallinity degree increases from 0.54 (original bamboo) to 0.64 (cellulose rich fraction). This is in good agreement with the experimental results described above, as hemicellulose and lignin (amorphous) are removed during the treatment and, therefore, the proportion of cellulose in this fraction increases; thus augmenting the degree of crystallinity of this fraction.

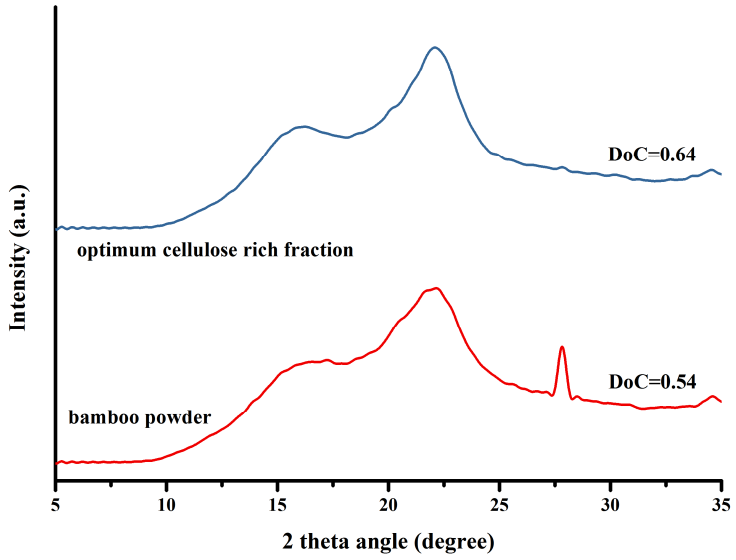

Figure 40: XRD patterns for the original bamboo powder and spent solid produced the optimum conditions.

3.5.5 Organosolv lignin as a sunscreen enhancer

In order to investigate the lignin sunscreen enhancement effect, four Nivea creams with different sun proofing factor (SPF) are prepared. And the bamboo organosolv lignin was blended into different creams separately. The SPF value for these creams are 0 (N-0),10 (N-10),30 (N-30),50 (N-50), respectively. Those creams as well as the lignin blended cream Figure 41 illustrated the different sun screen's UV proofing ability. It can be clearly seen that N-0 cream can barely screen any UV lights, and for N-10, N-30 and N-50, the UV screening effect is clearly stronger, at UVA band (320-400 nm) less than 1 % of UV light can penetrate N-10, N-30 and N-50. When blending 10 % (w.t.) lignin into the N-0 cream. The mixed cream UV screening ability is increased dramatically, but still not as good as those commercial sunscreens. The similar effect was also reported by Zhu et al. on lignin derived from other sources [203, 218].

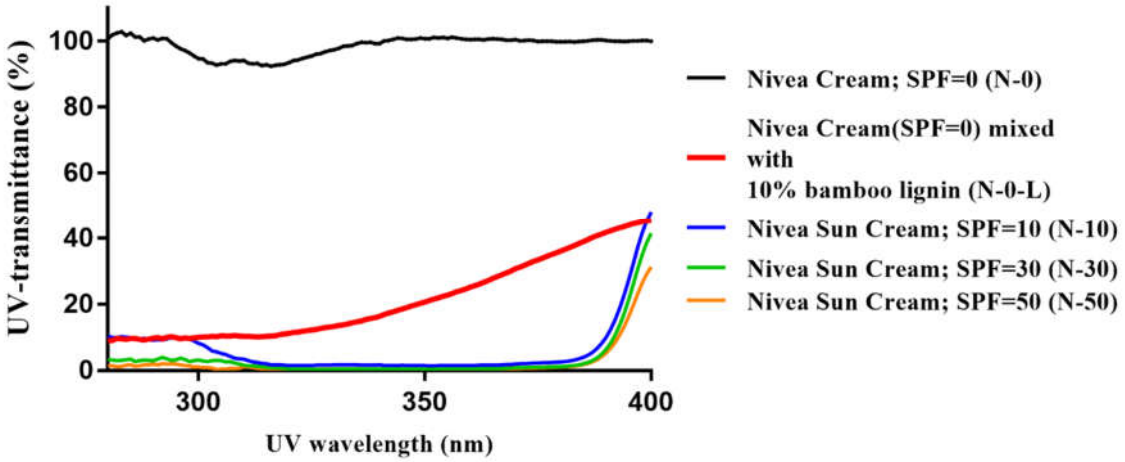

Figure 41: UV transmittance of Nivea cream with different SPF value and SPF 0 cream blended with 10% lignin (w.t.).

By comparing the N-10 and N-10 mixed with 10 % of lignin (N-10-L), it can be clearly seen that the sun screening ability for N-10-L is clearly enhanced in both UVA (320 – 400 nm) and UVB (280 – 320 nm) band (Figure 42). The similar trends are found in N-30 (Figure 43) and N-50 (Figure 44).

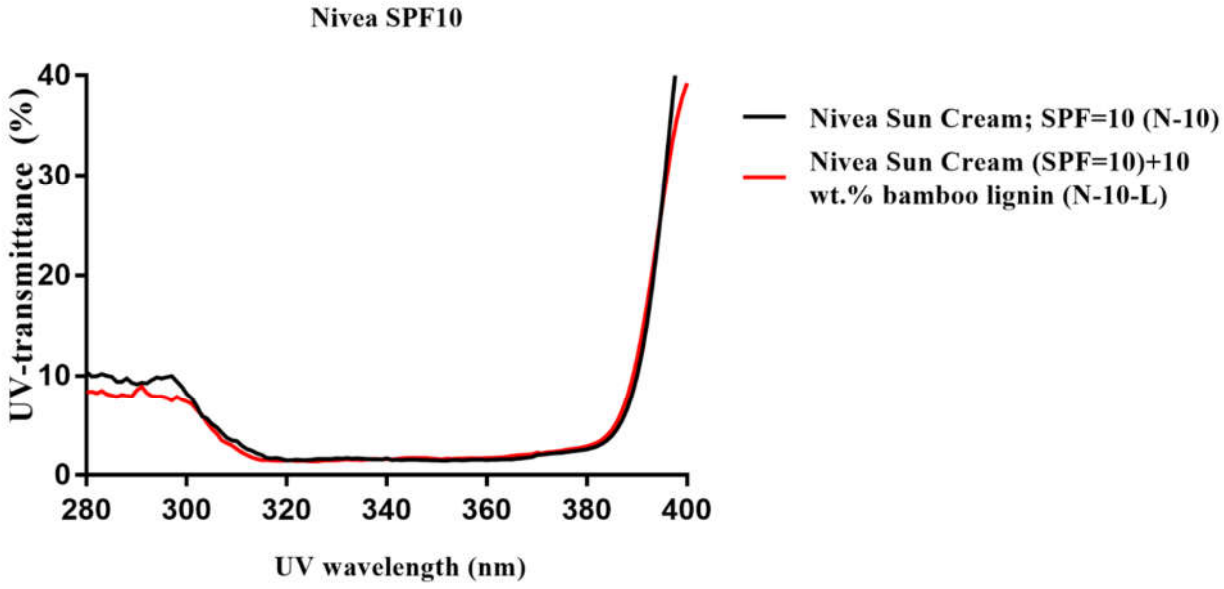

Figure 42: UV transmittance of Nivea sun cream (N-10) with and N-10+10 % lignin (w.t.)

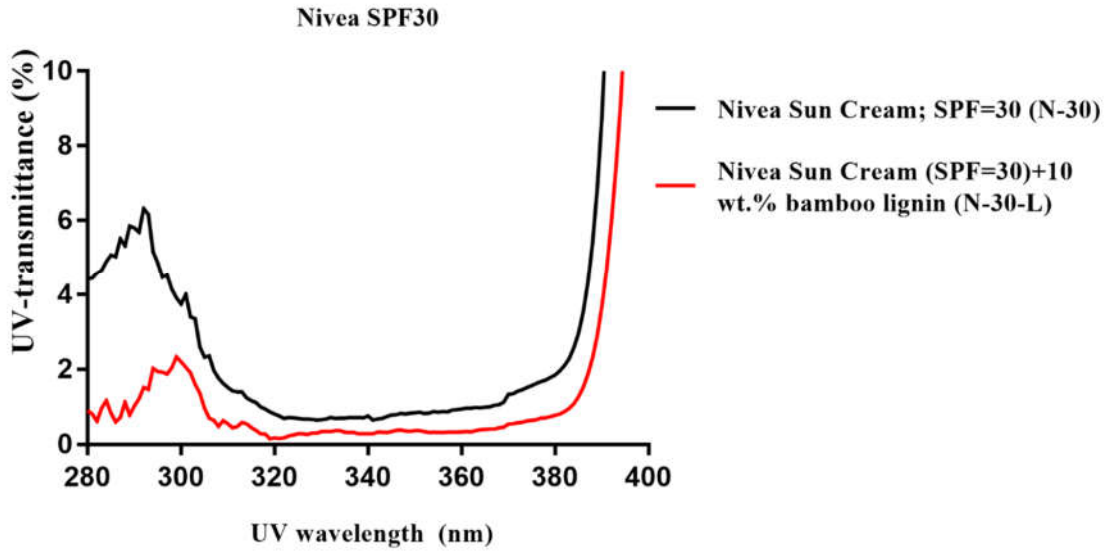

Figure 43: UV transmittance of Nivea sun cream (N-30) with and N-30+10 % lignin (w.t.)

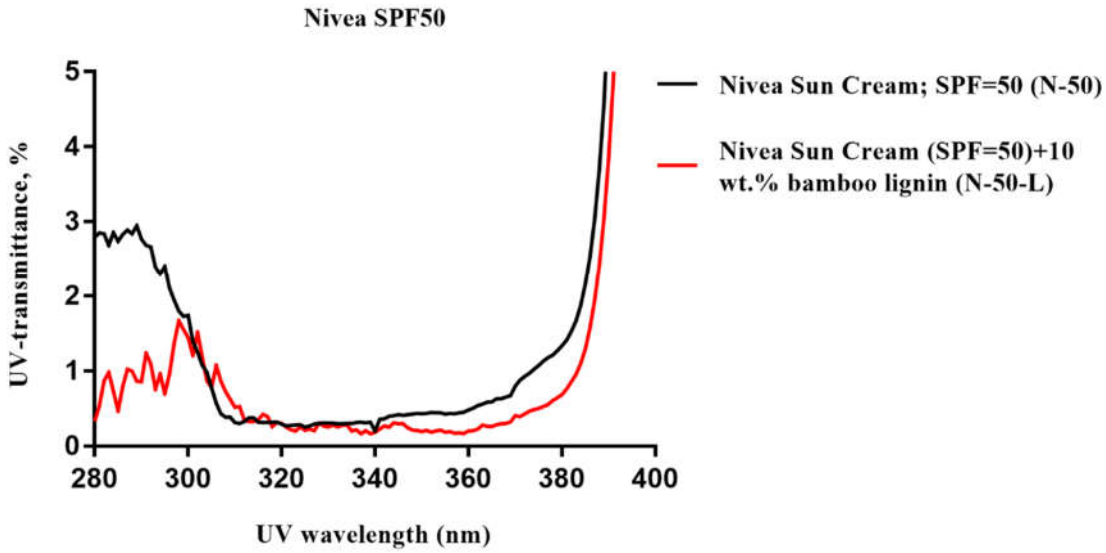

Figure 44: UV transmittance of Nivea sun cream (N-50) with and N-50+10 % lignin (w.t.)

The bamboo organosolv lignin can significantly improve the sun-screening ability for both pure cream (SPF=0) and commercial sunscreens, this result is in a good agreement with [203, 218]. This enhancement works for the entire range of UV spectrum (280 – 400 nm), especially in the UVB band. The UVB band is the main cause of skin reddening and sunburn, it plays a key role in the development of skin cancer and a contributory role in tanning and photoaging. Therefore, it is especially important to screen out the UVB band. And bamboo organosolv lignin is a good potential natural derived additive for sunscreen creams to enhance the screening ability of UVB band.

3.6 CONCLUSIONS

This work addresses a novel microwave-assisted, acid catalysed, organosolv process for the selective fractionation of bamboo analysing how and to what extent the reaction temperature (110-190 ºC), solvent system (EtOH/H_2O) and catalyst amount (0-5 vol.% formic acid) affect the yields and the most important properties of each fraction. The most important conclusions obtained from this work are summarised as follows.

1. The operating variables exert a significant influence on bamboo fractionation, with three main fractions being obtained: i) a cellulose-rich solid fraction, ii) a hemicellulose rich water-soluble fraction and iii) a lignin rich fraction. The yields to each one of these fractions varied by 51-94%, 2-23% and 2-32%, respectively.

2. Increasing temperature exerts a positive effect on bamboo decomposition, increasing the overall bamboo conversion. The effect of the concentration of ethanol in water (solvent system) depends on the temperature. At low temperature (110 ºC) the solvent system does not exert a very important influence, while a synergetic interaction between EtOH and H_2O takes place at high temperature, and better results are obtained with EtOH/H_2O mixtures

than with pure solvents alone. The effect of the catalyst is relatively weak, however it does demonstrate a noticeable effect when using a high temperature and high proportions of water in the solvent system.

3. The cellulose rich solid fraction consists of the solid residue obtained after the microwave treatment of bamboo, and it is made up of un-reacted cellulose (44-83 wt.%), hemicellulose (0-21 wt.%) and lignin (12-34 wt.%). The water-soluble hemicellulose rich fraction consists of a mixture of oligomers, sugars, carboxylic acids, ketones and furans. The relative amounts (in C basis) of these families of compounds vary by 0-100 wt.%, 0-100 wt.%, 0-100 wt.%, 0-13 wt.% and 0-4 wt.%, respectively. The solid rich lignin fraction comprises high pure (>95%) organosolv lignin, with a molecular weight range of 600 to 3177 Da.

4. An optimum for this bamboo fractionation process was found at 190 ºC using a solvent system consisting of 45% EtOH/50% H_2O (vol/vol) with a concentration of formic acid of 5 vol.%. These conditions maximise the solubilisation of lignin and hemicellulose in the organosolv system and minimise cellulose conversion; thus allowing the selective fractionation of bamboo into a high purity (84 wt.%) cellulose solid fraction, pure (>95%) organosolv lignin and a rich hemicellulose fraction consisting of a mixture of oligomers (27 C-wt.%), sugars (56 C-wt.%) and carboxylic acids (14 C-wt.%) in water.

5. The bamboo organosolv lignin shows a good potential to be an additive for commercial sunscreen cream.

Chapter 4. Microwave assisted Starbon® preparation: a mini project

The product of this chapter was supplied to Sigma Aldrich Co. as a commercial chemical.

4.1 SUMMARY

In this chapter, a novel microwave-assisted starch expansion method is described as an efficient starch expansion method for Starbon® preparation. Moreover, sulfolane (as a substitution for ethanol) is introduced as an alternative solvent for this process, which is widely used in the solvent exchange process for Starbon® production.

4.2 MESOPOROUS MATERIALS

Porous materials have significantly attracted increased scientific and technological interest because of their ability to interact with atoms, ions, and molecules not only at the surface, but also throughout the bulk of the material [219]. Therefore, porous materials are widely applied in adsorption, catalysis, and catalyst support processes [220]. According to their pore size, porous materials are classified into three major categories: micropore materials, mesopore materials, and macropore materials (Table 17).

From the green chemistry perspective, the production of traditional micropore materials is highly undesirable because the process involves a considerable number of complex steps, especially for the carbon materials production. Moreover, during the template removal process a lot of waste is generated [221]. Thus, these barriers add up to a costly and low resource efficiency process [222].

Table 17: Classification of porous materials.

Pore type	Pore size (nm)
Micropore	< 2
Mesopore	2 – 50
Macropore	> 50

4.3 STARCH AS A RAW MATERIAL TO PRODUCE MESOPOROUS MATERIALS

In general, materials can be obtained from three major sources, including minerals (gold, iron, silica etc.), fossil resources (natural gases, coal, crude oils), and biomass resources. Among these three major sources, only biomass resources are thought to be renewable. In recent years, bio-based materials have attracted much interest due to increasing concerns of human sustainability.

Polysaccharides are widely recognised as an inexpensive, non-toxic, bio-degradable, multifunctional, and widely available raw material for the production of bio-based materials [223]. Among all types of polysaccharides, starch is a key candidate to produce bio-based materials given their great potential for chemical modification and their availability all around the world. As mentioned in Chapter 1, a large amount of starch is currently being underutilised or wasted. For example, it has been reported that starches can be recovered from side stream processes in the potato industry such as, potato peeling, cutting, and waste potatoes from the manufacturing of potato crisps [224]. Recovering starches from underutilised streams may effectively prevent the conflict between utilising starch for chemical purposes and food requirement.

4.4 STARCH EXPANSION

To make full use of starch, additional treatments are required. Numerous starch processing methods are currently being utilised in industry. Among these processing methods, heating starch in an excess of water is the simplest and most common approach, in which varies physical properties within the starch granule are changed and gelatinisation is induced [225]. Starch gelatinisation is a process in which, in the presence of heat and water,

intermolecular bonds of starch are broken, leading to loss of starch crystallinity and simultaneous swelling of the starch granule [226]. A schematic overview of the gelatinisation process, which explains the starch granule swelling process and rupture of the final starch granule after maximum swelling is shown in Figure 45. One significant change from the starch granule's expansion was the increase of its surface area, which increased from less than 1 $m^2 g^{-1}$ to 100 – 180 $m^2 g^{-1}$ [221].

As a result, the porosity of the material dramatically enhanced [222]. The gelatinised starch was a near homogeneous, viscous, and aqueous solution. If, at this point, the mixture cooled down, there would be a strong force driving towards crystallisation. During the cooling process, amylose will rapidly form an elastic gel because of polymer aggregation. This process is known as retrogradation [227]. However, if the retrogradation process lasts too long, the gelatinised starch will collapse due to the interaction of starch with water. To maintain the increased surface area and porosity, water should be removed from the solution and replaced by solvents with a lower surface tension. Traditionally, ethanol was used as the substitution for water.

4.5 STARBON® DEVELOPMENT AND APPLICATION.

Starbon® is a mesoporous, templating agent-free, carbonaceous material developed by researchers from the Green Chemistry Centre of Excellence, University of York. The novel mesoporous material was made from a starch precursor. The production of Starbon® utilises the natural property of starch to form a nanochannel biopolymer structure when gelatinised in water, which may act as a natural templating agent [222]. The Starbon® production method is shown in Figure 46. The preparation of Starbon can be divided into three major steps:

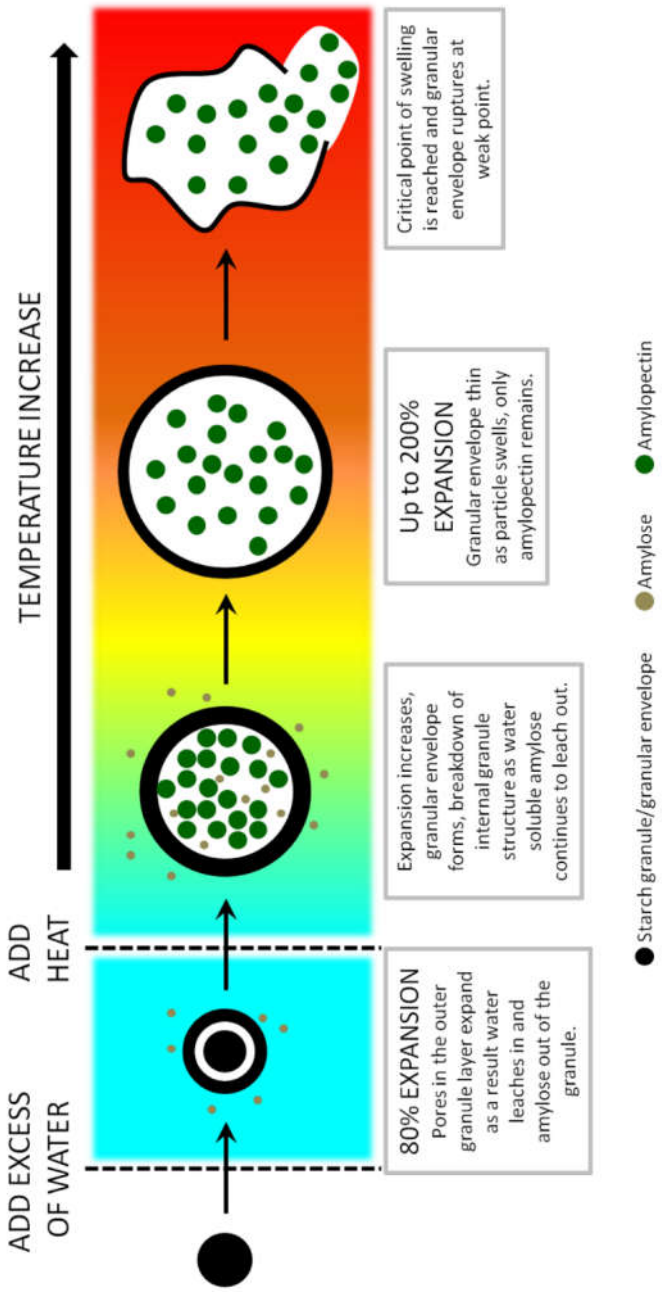

Figure 45: Molecular events during starch gelatinisation (Adapted from [221]).

1. Starch polymer expansion via polysaccharide aqueous gel preparation: this is the key process step and expands the structure of starch. A predominantly mesoporous pore network is built in this step.

2. Solvent exchange and drying process for mesoporous solid production: as stated before, water should be removed in the retrogradation process to prevent collapse of the porous polysaccharide structure. In this step, water is replaced by ethanol. The drying process is relatively simple, for starch, a vacuum oven effectively removes ethanol from the starch gel.

3. Carbonisation: after the solvent exchange and drying process, a mesoporous starch structure is formed temporally. However, the mesoporous structure is fragile, and when it absorbs water, the mesoporous structure will collapse. Various other conditions can destroy the mesoporous structure [228]. Therefore, to fix the mesoporous structure of expanded and dried starch-based materials, a thermolyzes process is required. The carbonisation process is catalysed using organic acid para-toluene sulfonic acid [222].

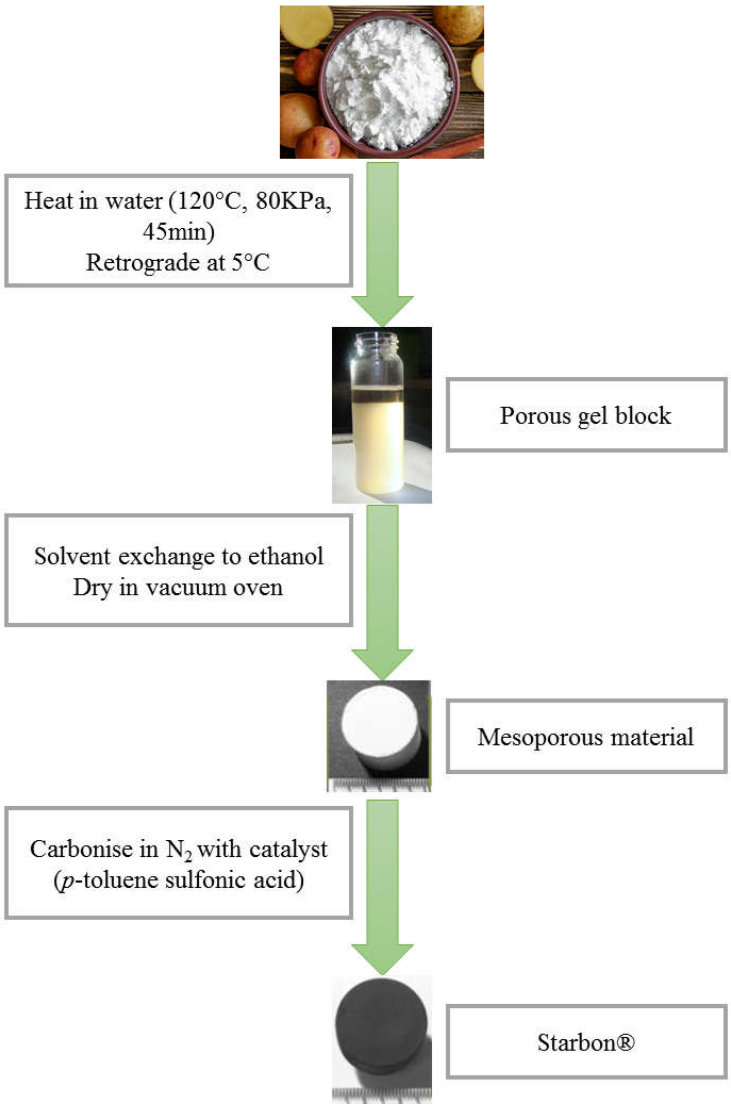

Figure 46: Conventional Starbon preparation process.

4.6 MICROWAVE-ASSISTED STARCH EXPANSION

During the starch expansion process, microwave heating was introduced as a more controllable and efficient alternative heating method. As mentioned in Chapter 1, microwave heating has many advantages, it is energy efficient, rapid, and highly controllable. During the conventional starch expansion process, it takes at least 45 min to

sufficiently expand the starch. However, when using the microwave-assisted starch expansion process, the target temperature could be reached in only 5 min. Moreover, after 10 min of holding time, the starch was perfectly expanded. Thus, due to these advantages, a microwave-assisted starch expansion method for Starbon production was established.

4.7 DETAILED MICROWAVE-ASSISTED STARBON® PRODUCTION

Corn starch (6g) was loaded onto 70ml of a CEM PrepPlus® reactor, containing 54ml of deionised water. The slurry was stirred and heated, using a microwave, to form a gel. The heating program was set as 5 min ramping time to achieve a temperature of 140°C and was subsequently set to hold for a total of 10 min. After gelation, the gel was immediately transferred and evenly sprayed onto a clean plastic tray. Next, the tray was stored at 4°C for 48 hours. The resulting mixture was cut into 2cm wide strips and transferred to a 2 L glass beaker, containing 1 L of sulfolane for solvent exchange. The mixture was stirred for 4 hours, then left to separate for 20 hours to form a clearly visible liquid and solid phase. Subsequently, the sulfolane was decanted off and the entire process repeated 3 times. The used sulfolane was carefully collected for future recycling use. For the last solvent exchange process, after stirring, instead of standing for 20 hours, the mixture was vacuum filtered by means of a sintered glass funnel to remove as much sulfolane as possible. To remove the remaining sulfolane, the filtered starch gel was placed in a vacuum oven at 80°C for 12 hours. After the vacuum drying process, the dried, expanded starch was soaked in *p*-toluenesulfonic acid at 5% (wt./wt.) and added to a 2 L flask containing 1 L of toluene. The system was fitted with a reflux apparatus and heated for 6 hours. To yield the Starbon® precursor, the resulting material was filtered and dried under vacuum in an oven at 80 °C.

The precursor was heated in a nitrogen atmosphere at 1°C min^{-1} to the targeted temperature, which, in this approach, was 300°C.

4.8 ADVANTAGES OF THE MICROWAVE-ASSISTED STARBON® PRODUCTION METHOD

A comparison between microwave-assisted starch expansion and traditional starch expansion is presented in Table 18.

Table 18: Comparison between microwave-assisted Starbon production and traditional Starbon production.

	Traditional Ethanol Starbon® production system	Microwave-assisted Sulfolane-Toluene Starbon® production system
Starch to water ratio	1:5	1:9
Heating temperature	120°C	140°C
Total heating time	45 min	15 min
Retrogradation	5°C	5°C
Solvent used for solvent exchange	Ethanol	Sulfolane
Solvent recycle	No	Yes
BET Surface area	>187 $m^2 g^{-1}$	>208.65 $m^2 g^{-1}$
Mesopore volume	0.2 $cm^3 g^{-1}$	0.69 $cm^3 g^{-1}$

From Table 18, that the Starbon® produced from microwave assisted production system had a higher BET (Brunauer-Emmett-Teller) surface area and greater mesopore volume compare to the Starbon® produced by traditional method.

In addition, due to microwave-assisted heating, the total heating time was reduced by 67%. Moreover, the total time saving as well as the higher heating efficiency, resulted in a significant saving in energy. In traditional Starbon production, at least 3 litres of ethanol are used [221]. Since no solvent recycling process was present, a significant amount of ethanol was wasted, which may potentially increase the environmental burden. However, when using the sulfolane method, over 90% of the sulfolane can be recycled, which results in a greener production process. Thus, sulfolane is a highly-stable and attractive alternative solvent. Compared to other solvents, sulfolane is more toxic, however, it has a very low skin penetration [229]. Moreover, a significant benefit was the high boiling point (285°C) of sulfolane, which caused it to be easily recovered from water by using vacuum distillation.

Chapter 5. Concluding remarks and future works

Converting naturally abundant and sustainable biomass as well as its major components with the assist of microwave heating technology into value-added chemicals and fuels, contributes a step forward towards a "greener" society. In the scope of this project, microwave assisted thermal conversion and/or valorisation of bamboo and beechwood xylan have been demonstrate to very good effect.

In Chapter 2, the microwave assisted pressurised, additive free, low temperature (< 250 °C) pyrolysis process allows for efficient conversion of beechwood xylan, the products (bio-gas, bio-oil and bio-char) distribution can be selective. The sample mass exerted a significant influence on the product distribution. Solid production is favoured using a low amount of hemicellulose. This resulted in up to 80 % conversion of the feedstock into bio-char. Conversely, a further increase in the amount of hemicellulose from 0.3 to 0.7 g led to a sharp increase in the yield of gas (40 %) and bio-oil (20 %) together with a decrease in the char yield (40 %). The effects of the mass loading accounted for by the different physical state (vapour or liquid) of the volatiles released during the pyrolysis reaction depend on the pressure reached during the experiment. Bio-oil as one of the most attractive product from pyrolysis was analysed. The bio-oil was made up of aldehydes, alkenes, phenols, polyaromatic hydrocarbons (PAHC), cyclic ketones and furans, having a composition dependent on the mass of hemicellulose employed. The solid residue (bio-char) has a higher proportion of carbon together with a lower proportion of oxygen than the original feedstock, which leads to a considerable increase in its higher heating value (HHV) in comparison to xylan. In addition, the char produced using fast heating had a decarboxylation/dehydration ratio slightly higher than that produced under slower heating

rate condition. The pyrolysis process leads to energy efficiencies of 100 and 26 % for char and bio-oil production, respectively. This caused to an increase in the HHV (compare to the original feedstock) of 43 % for char and 19 % for bio-oil.

In Chapter 3, the microwave assisted organosolv of one of the fastest growing nature biomass, bamboo, has demonstrated a potential of selective fractionate biomass efficiently. In order to investigate the influence of the reaction temperature (110 – 190 °C), ethanol concentration in water (0 – 100 vol. %) and catalyst (formic acid) loading (0 – 5 vol. %) on the fractionation of bamboo under microwave irradiation. A two level, three factor, Box-Wilson Central Composite Face Centred (α: ±1) design was used. The experimental results were analysed with an analysis of variance (ANOVA) with 95 % confidence and the cause-effect Pareto principle to determine the relative influence of the operating variables and optimise the process towards a selective fractionation.

Three major fractions are produced from the organosolv process, they are cellulose-rich solid fraction, hemicellulose rich water-soluble fraction and a lignin rich fraction. The synergetic effect of these three factors on the fractionation process was studied.
According to the statistical analysis, an overall optimum for bamboo fractionation was found at 190 °C using a solvent system consisting of 45 % EtOH/50 % H_2O (vol/vol) with 5 vol. % formic acid. In this condition, the solubilisation of lignin and hemicellulose is maximised, while the cellulose conversion is minimised. Under this condition, a 84 wt.% cellulose solid fraction, pure lignin fraction (> 95 %) and a hemicellulose rich fraction can be produced. An application of using the organosolv lignin as an enhancer for commercial

sunscreens is tested. Bamboo organosolv lignin shows a good potential in blocking the UV lights, in particular in the UVB spectrum range.

In Chapter 4, a microwave assisted Starbon® producing method is reported. By using this method, significant amount of operation time and energy could be saved due to the special microwave heating mechanism. Sulfolane has been introduced as an alternative solvent to substitute ethanol, which was widely used in traditional Starbon® make process to eliminate water in the expanded starch. Sulfolane as a solvent with high boiling point can be recycled easily by simple vacuum evaporation, resulting in a significant reduction in total amount of solvent wasted. Thus, the overall production procedure is more environmental friendly.

In the future, more investigation should be carried out on the pressure influence of microwave assisted pyrolysis of other biomass, as this is a low-cost, doping free way to achieve selective pyrolytic product distribution. The methodology used in bamboo organosolv should be promoted to other biomass biorefinery process to determine the optimum reaction condition for the biorefinery process. Microwave assisted heating could be applied to more traditional manufacturing process as a more efficient substitute heating method.

Overall, I believe that microwave assisted biorefinery has a bright future. In my opinion, the future direction of this area will be focusing on the commercialisation of microwave biorefinery technologies. Currently, several barriers are affecting the commercialisation of microwave assisted biorefinery.

The first barrier is that microwave radiation requires specialised reactor system. The specialised microwave reactor could make the factories' overhead cost significantly higher than using conventional reactors. The other barrier is microwave assisted biorefinery process should undergo several additional safety regulations before the technology could be commercialised. The third barrier is the products quality and stability. If I have the opportunity in the future, I will probably collaborate with experienced engineering team to design less expensive, easy to operate, and safe as well as reliable microwave reactors to meet the market needs and safety regulations. I might also continue my research in collaboration with companies to design an industrial scale microwave assist biorefinery production line to produce useful microwave assisted biorefinery products.

Abbreviations

AFEX	-	Ammonia Fibre Explosion
ANOVA	-	Analysis of Variance
AR	-	Analytical Reagent grade
BET	-	Brunauer Emmett Teller
CCF	-	Composite Face Centred
DP	-	Degree of Polymerisation
DTA	-	Differential Thermal Analysis
DoC	-	Degree of Crystallinity
dTG	-	differential Thermal Gravimetric
EC	-	Earth's Capacity
EPA	-	Environmental Protection Agency
EtOH	-	Ethanol
EU	-	European Union
FT	-	Fourier Transform
GC	-	Gas Chromatography
GPC	-	Gel Permeation Chromatography
GVL	-	γ-valerolactone
HHV	-	Higher Heating Value
HPLC	-	High Performance Liquid Chromatography
HSP	-	Hansen Solubility Parameters
HSQC	-	Heteronuclear Single-Quantum Coherence
ICP	-	Inductively Coupled Plasma

Indep.	-	Independent
IR	-	Infrared spectroscopy
ISO	-	International Organisation for Standardisation
LCF	-	Lignocellulosic Feedstock
LSD	-	Least Significant Difference
MCT	-	Mercury Cadmium Telluride
MS	-	Mass Spectrometry
PAHC	-	Polyaromatic Hydrocarbons
PTFE	-	Polytetrafluoroethylene
SEM	-	Scanning Electron Microscopy
SPF	-	Sun Proofing Factor
STA	-	Simultaneous Thermal Analysis
STP	-	Standard conditions for Temperature and Pressure
TC	-	Total Carbon
TG	-	Thermal Gravimetric
THF	-	tetrahydrofuran
TIC	-	Total Inorganic carbon
TOC	-	Total Organic Carbon
ROI	-	Return on Investment
UN	-	United Nations
UNEP	-	United Nations Environment Programme
US	-	United States
UV	-	Ultraviolet

UVA	-	Ultraviolet A
UVB	-	Ultraviolet B
VIS	-	Visible
VK	-	Van Krevelen
XRD	-	X-ray Diffraction

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Appendix:

APPENDIX A: "12 GUIDING PRINCIPLES OF GREEN CHEMISTRY"

The "12 guiding principles of green chemistry" are as follows:

1. **Prevention**

   It is preferred to prevent waste than to treat or clean up waste after it has been created.

2. **Atom Economy**

   Synthetic methods should be designed to maximise the incorporation of all materials used in the process to generate the final product.

3. **Less Hazardous Chemical Syntheses**

   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals**

   Chemical products should be designed to affect their desired function while minimising their toxicity.

5. **Safer Solvents and Auxiliaries**

   Wherever possible, the use of auxiliary substances (e.g., solvents, and separation agents) should be made unnecessary and innocuous when used.

6. **Design for Energy Efficiency**

   Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstocks**

   Whenever technically and economically practicable, a raw material or feedstock should be renewable rather than depleting.

8. **Reduce Derivatives**

   If possible, unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimised or avoided because such steps require additional reagents and can generate waste.

9. **Catalysis**

   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation**

    Chemical products should be designed in such a fashion that at the end of their function they break down into innocuous degradation products, and do not persist in the environment.

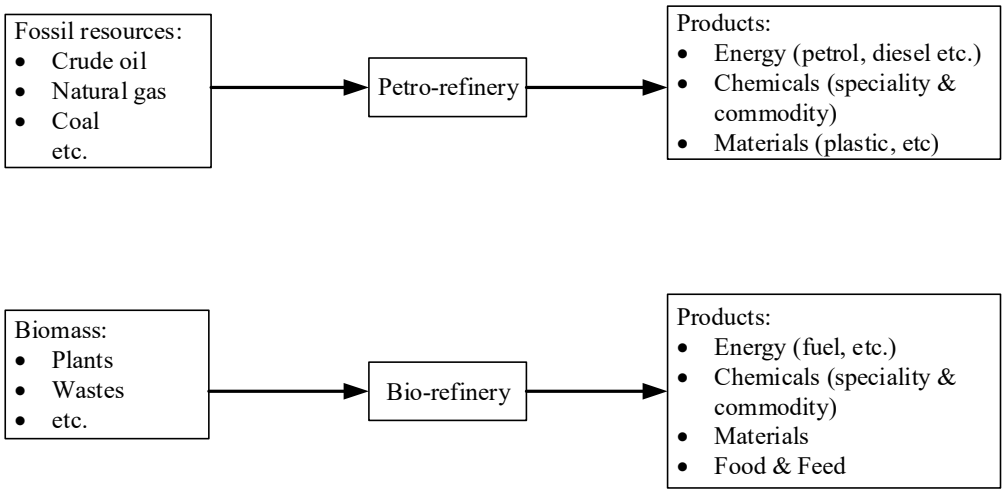
11. Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions, and fires.

APPENDIX B: COMPARISON BETWEEN PETRO-REFINERY AND BIO-REFINERY



Comparison between petrol-refinery and bio-refinery.

APPENDIX C: A DETERMINATION OF THREE MAIN CHEMICAL COMPOSITION CONTENTS IN BIOMASS

Experimental design

Cellulose, hemicellulose, and lignin are major organic components of the cell wall of plants. Cellulose is involved in the formation of microfibers and makes up the reticular skeleton of the fiber cell wall, whereas hemicellulose and lignin act as "adhesives" and "fillers", and fill up the spaces between fibers and microfibers.

Cellulose

During the heating process, biomass powder is allowed to react with a mixed solution of acetic acid and nitric acid. Under these circumstances, intercellular substances are dissolved and cellulose is broken up into single fibers. Lignin, hemicellulose, and other substances are removed. Starch, pentosan and other substances are hydrolyzed. After impurities are washed and removed by water, cellulose is oxidized to carbon dioxide and water by potassium dichromate in the presence of sulfuric acid according to the following reaction:

$$C_6H_{10}O_5 + 4K_2Cr_2O_7 + 16H_2SO_4 = 6CO_2 + 4Cr_2(SO_4)_3 + 4K_2SO_4 + 21H_2O$$

Surplus potassium dichromate is titrated by ammonium ferrous sulfate solution. Then, a same amount of potassium dichromate that has not reacted with cellulose, is titrated by ammonium ferrous sulfate. The cellulosic contents can be obtained based on difference values.

Hemicellulose

Fully dissolve starch in a boiling, 80 (wt.) % calcium nitrate solution. This step assures that other water-soluble carbohydrates that interfere with the determination of hemicellulose shall be removed. After the sediment is washed using distilled water, the hydrolytic time of hemicellulose will be greatly shortened when using high-concentration hydrochloric acid. The sugar solution that is obtained via hydrolysis will be neutralized by sodium hydroxide solution after being diluted to a certain volume. The total sugar content is determined via a copper and iodine approach.

Principle of the copper and iodine method: When cupric sulfate is converted to cuprous oxide by sugar that is generated after hydrolyzed hemicellulose under alkaline conditions and is being heated, the cuprous oxide will precipitate in the form of Cu_2O. The quantity of Cu_2O is determined by the copper and iodine method, in which the contents of hemicellulose are calculated.

Next, the KIO_3 and KI contents that are contained in the copper base reagent of reduced sugar will be determined. KIO_3 and KI will react under acidic conditions but do not interfere with the reaction between the sugar and copper ions. After the addition of acid, KIO_3 and KI will react and iodine is released as follows:

$$KIO_3 + 5KI + 3H_2SO_4 = 3I_2 + 3K_2SO_4 + 3H_2O$$

After the addition of oxalic acid, iodine will react with cuprous oxide as follows:

$$Cu_2O + I_2 + H_2C_2O_4 = CuC_2O_4 + CuI_2 + H_2O$$

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

Excessive iodine will be titrated by $Na_2S_2O_3$ solution: $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$

Lignin

Sugar, organic acid, and other soluble compounds can be extracted after treatment with 1% acetic acid. Then, chlorophyll, fat-like substances, lipids, and other fat-soluble compounds can be extracted after treatment with acetone. After washing the sediment with distilled water, any lignin that is present in the hydrolysate is oxidized by potassium dichromate in the presence of sulfuric acid as follows:

$$C_{11}H_{12}O_4 + 8K_2Cr_2O_7 + 32H_2SO_4 = 11CO_2 + 8K_2SO_4 + 8Cr_2(SO_4)_3 + 32H_2O$$

Excessive potassium dichromate is titrated by ammonium ferrous sulfate solution. This method is similar to the method that is used for the determination of cellulose.

Reagents and instruments

Reagents

Ammonium ferrous sulfate, (AR); potassium dichromate, (AR); sodium thiosulfate, (AR);

Calcium nitrate, (AR); copper sulfate, (AR); soluble starch, (AR);

Potassium iodate, (AR); oxalic acid, (AR); tartaric acid, (AR);

Barium chloride, (AR); phenanthroline, (AR); concentrated sulfuric acid, (AR);

Hydrochloric acid, (AR); glacial acetic acid, (AR); nitric acid, (AR).

Instruments

50mL acid burette, 50mL base burette, several 10mL centrifuge tubes, beakers of different sizes;

stoppers, several 250mL conical flasks, heating plates, high-speed centrifuge.

Experimental steps

Cellulose content determination

1.Required solutions:

Mixture of nitric acid and acetic acid, potassium dichromate solution (0.5N), ferroin indicator.

0.1N ammonium ferrous sulfate solution, concentrated sulfuric acid, potassium dichromate solution (0.1N).

2. Experimental steps

（1） Prepare all required solutions ahead of time. The ammonium ferrous sulfate solution shall be used within a week after preparation and the titer (K) shall be determined on the day of the experiment. Potassium dichromate solution (25mL 0.1N) is titrated by ammonium ferrous sulfate solution and ‘m’ mL is applied.

$$K= 25\times0.1/m$$

（2） Weigh natural withering biomass powder 0.05-0.06 g, the value of the weight is

presented as ‘n’.

（3） Transfer the biomass powder to a centrifuge tube and add 5mL of a mixture containing nitric acid and acetic acid.

（4） Secure the centrifuge tube and incubate this in boiling water for 25 min, stirring at regular intervals is recommended.

（5） Centrifuge at 3500 rpm for 10 min and discard the supernatant and add distilled water for centrifugation, washing and sedimentation. Repeat this step 3 times.

（6） Add 10 mL of 0.5 N potassium dichromate solution and 8 mL of concentrated sulfuric acid for uniform blending. Place the tube in boiling water and incubate for 10 minutes, stir at regular intervals.

（7） Cool and pour the solution into a conical flask and wash and precipitate using distilled water and 3 drops of ferroin indicator solution. The solution is titrated using 0.1N ammonium ferrous sulfate solution and ‘b’ mL is applied. The endpoint is determined when the solution changes color from yellow to kelly (green).

（8） Ammonium ferrous sulfate solution (0.1N) is used for a separate titration. Add 8mL of concentrated sulfuric acid and 10 mL of 0.5N potassium dichromate solution and ‘a’ mL is applied

（9） The formula to calculate the cellulosic content (x) in the biomass is as follows:

$$x\% = 0.675 \times K \times (a - b)/n$$

Hemicellulose content determination

1. Required solutions

Calcium nitrate solution (80 %), hydrochloric acid (2N), phenolphthalein indicator, sodium hydroxide solution (2N), basic copper reagent.

Oxalic acid-sulfuric acid mixed solution, 0.5% starch, sodium thiosulfate solution (0.01N).

2. Experimental steps

（1） Weigh natural withering biomass powder 0.1-0.2 g, the value of the weight is presented as ‘n’.

（2） Transfer the biomass powder to a small beaker, add 15mL of 80% calcium nitrate solution, cover the beaker and keep the mixture boiling for 5 minutes.

（3） The biomass sediment is washed by 10 ml hot distilled water each time and precipitated by centrifuge at 3500 rpm for 7 min. And repeat this process for three times.

（4） Add 10mL of 2N hydrochloric acid to the sediment for uniform blending. The sediment is slightly boiled for 45 minutes under blending conditions in a water bath containing boiling water.

（5） After centrifugation, the residues are washed 3 times by 10mL of distilled water. After washing, the solutions are merged.

（6） Add 1 drop of phenolphthalein and use a 2N sodium hydroxide solution to neutralize the solution until the color changes to orange-red.

（7） The solution is transferred into a 100mL volumetric flask and diluted to the volume.

（8） The solution is filtrated into a dry beaker by using dry filter paper.

（9） A total of 10mL filtrate is removed by a pipette and 10mL of basic copper carbonate is added. The flask is covered and the mixture is heated for 15 minutes in a water bath containing boiling water.

（10）Cool the mixture down and add 5mL of oxalic acid-sulfuric acid solution, then add 0.5mL of 0.5% starch. Next, 0.01N sodium thiosulfate solution is used for titration until the blue color fades away. A total of ‘b’ mL is applied.

（11）Take 10mL of basic copper reagent, add 5mL of oxalic acid-sulfuric acid mixed solution, then add 10mL of filtrate and 0.5mL of 0.5% starch. Sodium thiosulfate solution (0.01N) is used for titration until the blue color fades away. A total of ‘a’ mL is applied.

（12）The formula for the calculation of hemicellulose content (x) in the biomass is as follows:

$$x\% = 0.9\times100\ [\ 248-(a-b)] \times (a-b)/10000\times10\times n$$

Lignin content determination

1. Required solutions

Acetic acid (1%), acetone, 73% sulfuric acid, 10% barium chloride solution, 0.5N potassium dichromate solution.

Concentrated sulfuric acid, 0.1N ammonium ferrous sulfate solution, ferroin indicator.

2. Experimental steps

（1） Demarcate the freshly-prepared 0.1N ammonium ferrous sulfate solution, the titer

is K.

（2） Weigh natural withering biomass powder 0.05-0.1g, the weight is presented as ‘n’.

（3） Transfer the biomass powder to a centrifuge tube, add 10mL of 1% acetic acid, and incubate under shaking for 5 minutes until they are evenly blended.

（4） After centrifugation, the sediment is washed by 5mL of 1% acetic acid solution.

（5） Add 3-4mL of acetone, soak for 3 minutes under shaking conditions, and wash with water for 3 times.

（6） Using a glass rod, the sediment is dispersed along the tube wall. Next, the centrifugation tube is placed in hot water to allow the sediment to dry.

（7） Add 3mL of 73% sulfuric acid to the dry sediment, and blend the mixture to a homogeneous phase by glass rod.

（8） Incubate overnight at room temperature.

（9） Add 10mL of distilled water for uniform blending and place the solution in boiling water for 5 minutes.

（10）Cool the solution and add 0.5mL of 10% barium chloride solution for uniform blending, then centrifuge at 3500 rpm for 10 min. The supernatant is discarded and the sediment is washed twice by 10mL of distilled water.

（11）Add 10mL of 0.5N potassium dichromate solution and 8mL of concentrated sulfuric acid to the sediment. Then, place the solution in boiling water and incubate, under occasional stirring, for 15 minutes.

（12）Cool the solution and pour it into a conical flask. Wash and precipitate the sediment using distilled water and 3 drops of ferroin indicator solution. The sediment is titrated by using 0.1N of ammonium ferrous sulfate solution and ‘b’ mL is applied.

The colour of the solution would change from yellow to yellow-green till bronze, which is the ending point of the titration.

（13）For a separate titration, 0.1N ammonium ferrous sulfate solution is used. Add 8mL of concentrated sulfuric acid and 10mL of 0.5N potassium dichromate solution and ‘a’ mL is applied.

（14）The formula for calculating the lignin content (x) in the biomass is as follows:

$$x\% = 0.433 \times K(a - b)/n$$