The potential for recovery of nutrients from biomass by hydrothermal processing

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1. The candidate performed nutrient recycling by microalgae cultivation. Dr Onwudili, Prof Williams, Dr Lea-Langton, Dr Camargo-Valero and Dr Ross contributed with comments, guidance and proof reading.
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Abstract

Hydrothermal processing has received increased interest mostly in the area of waste conversion to higher density fuels. However in addition to energy generation from these materials, it has become a promising route for nutrient extraction and recovery from either the solid or aqueous products depending on the processing temperature. This research was carried out in phases with the aim to improve extraction of nitrogen and phosphorus from various nutrient-rich wet wastes and the potential to recover these nutrients by biological means or by adsorption unto biochar.

The initial study was on various hydrothermal processing routes – thermal hydrolysis (TH), hydrothermal carbonisation (HTC), hydrothermal liquefaction (HTL) and supercritical water gasification (SCWG) at 170°C, 250°C, 350°C and 500°C respectively using high moisture and high nutrient feedstocks namely microalgae, digestate, swine manure and chicken manure. Experiments were conducted with 10:1 water: solid ratio and 1 hour residence time except for SCWG which was 30 minutes with 15:1 water: solid ratio. The fate of N, P and other inorganics from each feedstock during these processes were investigated as well as the product yields, composition of the aqueous products and solid products. The results indicate that feedstocks behave differently during hydrothermal processing with the composition and yields of by-products depending largely on feedstock composition and processing temperature. Highest solid yields were obtained at lowest temperatures while highest gas yields were obtained at the highest temperature. HTL favour formation of highest biocrude. Aqueous products from lower temperatures contain higher P levels (mainly organic-P and less phosphate) and lower N levels (mainly organic-N and less NH_3-N). At higher temperature it is vice versa. Extracted P depends on Ca, Mg and Fe in unprocessed feedstock. P is immobilised in solid product at higher temperatures. TOC in aqueous product decrease with increasing processing temperature.

The effect of additives on nutrient extraction during low temperature processing – Thermal hydrolysis at 120°C and 170°C as well as HTC at 200°C and 250°C using different reagents - alkali (0.1M NaOH), mineral acid (0.1M H_2SO_4) and organic acids, (0.1M CH_3COOH and 0.1M HCOOH) was investigated. All experiments were performed with 10:1 water: solid ratio in high pressure 600 mL Parr batch reactor for 1 hour. The nutrient mass flow balance during these processes, the composition of the aqueous product and solid products were investigated. The results indicate that TN is significantly affected by temperature rather than pH. NH_3-N in aqueous product increases with increasing temperature while organic- N reduces. Phosphorus extraction is pH and temperature dependent and further enhanced with additives. Acidic conditions favour phosphorus extraction especially with H_2SO_4 at all temperatures; highest (94%) extracted using H_2SO_4 at 170°C and presents opportunity for nutrient recovery. Neutral or basic conditions immobilise P in hydrochar and offers potential route for manure management as P-loss is reduced in the environment. Mg, Na and K are mostly extracted into aqueous product, while Ca and P concentrate in solid product as temperature increases. Acidic conditions extracted higher levels of micronutrient compared to water or NaOH. Generally micronutrients were more in the solid for most additives except H_2SO_4 while Ni and Al were mostly in the solid products.

Microwave pre-treatment of various feedstocks such as sewage sludge, microalgae, digestate and manures was performed with 15:1 water: solid ratio at 120°C for 15 minutes. Also the influence of additives on nutrient extraction from swine manure was also investigated. Results show that aqueous products contain significant levels of N and P; nitrogen mainly as organic-N rather than NH_3-N for all feedstock while it was mainly as organic-P for sewage sludge and digestate and more as phosphate with microalgae and manures. High TP was extracted with acidic reagents rather than with water or NaOH. With most additives, N in aqueous product was mainly as organic-N than NH_3-N while P in the aqueous product was mainly as phosphate rather than organic-P. Aqueous products contain most K and Na while the residues contain most Ca, Mg, P and micronutrients for most feedstocks. Acidic conditions most especially with H_2SO_4 extracted more Ca, Mg, P, Co, Mn, and Zn unlike neutral or alkaline conditions. In comparison with conventional heating, microwave heating generally extracted more nitrogen and phosphorus into the aqueous products.

Biological recovery of nutrients using various SCWG aqueous waste streams showed significant autotrophic growth of *Chlorella* in the diluted aqueous products except for the aqueous product from SCWG of *Chlorella* diluted at 1:50. *Chlorella* was able to utilise ammonium as a source of nitrogen. Higher dilutions of 1:400 had insufficient nutrients to promote growth. Biomass obtained from 1:50 dilution of catalysed SCWG of *S. latissimi*, *L.digitata*, sewage sludge and 1:200 dilution of SCWG *Chlorella* were comparable with biomass obtained using the standard Bold's Basal Media. The recovered biomass could be used as feedstock for biodiesel or lipid extraction. Physical recovery of phosphate from H_2SO_4 extracted aqueous products by adsorption using Mg-modified biochar shows that phosphate adsorption is affected by concentration and pH. Highest adsorption was achieved with 250 mg/L while higher adsorption efficiency was achieved at pH 8 and 9 compared to pH 7, precipitating more calcium phosphate on the biochar. Phosphate adsorption did not occur at lower/acidic pH conditions. There was no likelihood of struvite precipitation as EDX analysis showed no additional nitrogen and Mg in the adsorbed chars.

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List of Abbreviations

A

AD	Anaerobic Digestion
Al	Aluminium
As	Arsenic
ATP	Adenosine triphosphate

B

B	Boron
BBM	Bold’s Basal Media
BOD	Biological oxygen demand

C

C	Elemental Carbon; with catalyst
C2-C3	Alkane
C_2H_4	Ethylene
$C_6H_{12}O_6$	Glucose
Ca	Calcium
Ca^{2+}	Calcium ion
$Ca_3(PO_4)_2$	Calcium phosphate precipitate
$Ca_5(PO_4)_3(OH)$	Hydroxyapatite
$CaCO_3$	Calcium carbonate
$CaHPO_4.2H_2O$ / $CaHPO_4$	Dicalcium phosphate
CAFOs	Concentrated animal feeding operations
$Ca(OH)_2$	Calcium hydroxide
CCAP	Culture collection of algae and protozoa
Cd	Cadmium
CH_3COOH	Acetic acid
CH	Conventional heating
CH_4	Natural gas/ Methane
Cl	Chlorine
Co	Cobalt
CO	Carbon monoxide
COD	Chemical oxygen demand
CO_2	Carbondioxide
$CO(NH_2)_2$	Urea
Cr	Chromium
Cu	Copper

D

db	Dry basis
DNA	Deoxyribonucleic acid

E

EBPR	Enhanced biological phosphorus removal
EDS/EDX	Energy dispersive X-ray spectroscopy

F

Fe	Iron

G

GHG	Greenhouse gases

H

H^+	Hydrogen ion
H_2	Hydrogen gas
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid

$H_2PO_4^-$ or HPO_4^{2-}	Inorganic orthophosphate
H_2O	Water
H_3PO_4	Phosphoric acid
HCl	Hydrochloric acid
HCOOH	Formic acid
HFCs	Hydrofluorocarbon
Hg	Mercury
HHV	Higher heating value
HTC	Hydrothermal carbonisation
HTL	Hydrothermal liquefaction

I

IC	Inorganic carbon
ICP-OES	Inductively coupled plasma optical emission spectrometry

J

K

K	Potassium
K^+	Potassium ion
K_2O	Potash
K_2CO_3	Potassium carbonate
$KHCO_3$	Potassium bicarbonate
KOH	Potassium hydroxide

L

LED	Light emitting diode

M

Mg	Magnesium
Mg^{2+}	Magnesium ion
$Mg_3(PO_4)_2$	Magnesium phosphate
Mn	Manganese
Mo	Molybdenum
MW	Microwave heating

N

N	Nitrogen
Na	Sodium
Na^+	Sodium ion
Na_2CO_3	Sodium carbonate
NaOH	Sodium hydroxide
NC	Without catalyst
N_2	Nitrogen gas
N_2O	Nitrous oxide
NH_3	Ammonia
NH_3-N	Ammoniacal nitrogen
NH_4^+	Ammonium ion
NH_4^+	Ammonium nitrogen
NH_4NO_3	Ammonium nitrate
$(NH_4)_2\ SO_4$	Ammonium sulphate
$NH_4MgPO_4.6H_2O$	Struvite
Ni	Nickel
NO_3^-	Nitrate
NO_2^- -N	Nitrite nitrogen
NO_3^- -N	Nitrate nitrogen

O

O	Elemental oxygen

O_2	Oxygen gas
OH^-	Hydroxyl ion
OM	Organic matter
P	
P	Phosphorus
P_2O_5	Phosphorus pentoxide
Pb	Lead
PFCs	Perfluorocarbon
PO_4^{3-}	Reactive phosphate
PO_4^{3-} - P	Phosphate P
Q	
R	
RP	Reactive phosphorus
RNA	Ribonucleic acid
Ru/Al_2O_3	Ruthenium Alumina
S	
S	Sulphur
SO_3^{2-}	Sulphite
SO_4^-	Sulphate
SAMS	Scottish Association of Marine Sciences
SCWG	Supercritical water gasification
SEM	Scanning electron microscopy
Si	Silicon
T	
TC	Total carbon
TGA	Thermogravimetric analysis
TH/HYD	Thermal hydrolysis
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
U	
V	
VSS	Volatile suspended solids
W	
WAS	Waste activated sludge
X	
XRD	X-ray diffraction
Y	
Z	
Zn	Zinc
$ZnCl_2$	Zinc chloride

Chapter 1 Introduction

1.1 Challenges facing the fertiliser industry

One of the problems facing the fertiliser industry is the increasing demand for fertilisers with limited available raw materials for adequate supply. In the last decade, the production of fertilisers have increased in order to sustain large scale production of food for a growing world population. Dependence on fertilizers to maintain soil fertility by enhancing crop yields or even reviving nutrient deficient farmlands have also increased as only very few agricultural soils are regarded as being fertile (Dawson and Hilton, 2011). Unfertile soils need to be managed by periodic treatments with essential macronutrients such as nitrogen (N), phosphorus (P) and potassium (K), calcium (Ca), magnesium (Mg), sulphur (S) and other micronutrients such as chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), boron (B) and molybdenum (Mo) could also be added in smaller concentrations. Although among these nutrients, the role of N, P and K is the most crucial to ensure food security. Plants take up nitrogen in inorganic forms such as ammonium ion (NH_4^+) and nitrate (NO_3^-) using their roots. In 2010, the consumption of raw materials for chemical fertilizer production was as high as 2.7 Mt of potash (K_2O), 2.4 Mt of phosphate (P_2O_5) and 10.4 Mt of nitrogen (N) and was projected to increase to 3.2 Mt, 2.7 Mt and 10.8 Mt respectively by year 2019/2020 (Fertilizers Europe, 2010).

Fertilisers are manufactured commercially in a wide variety of compositions and concentrations. Phosphorus is usually expressed in terms of the quantity of available phosphate P_2O_5 where elemental P is about 44%. Elemental K is about 83% and is expressed as the quantity of soluble potash (K_2O). For instance a 5-10-5 fertiliser contains 5% total nitrogen, 10% available phosphoric acid and 5% soluble potash with micronutrients, macronutrients and other inactive ingredients accounting for the remaining 80% (Gellings and Parmenter, 2004). Compared to a 15-30-15 labelled fertiliser, it contains three times less nutrients even though the ratio of NPK is maintained.

Among other vital nutrients used in making fertilisers, phosphorus is limited while nitrogen is readily available in the atmosphere as nitrogen gas and potash is readily available ore. Phosphorus is mainly sourced from non-renewable phosphate rocks which are mined globally to meet phosphate demand. Although in the last decade, sedimentary rocks supplied 80-90% phosphorus needed while igneous rocks supplied 10-20% (FAO, 2004). In 2007 and 2008, the phosphorus market experienced huge price fluctuations with about 900% increase in price. This was thought to be a warning signal towards phosphorus rock scarcity (Heckenmuller et al., 2014). Since then emerging literature have predicted a time when 'peak phosphorus' production would occur. Some have predicted year 2033 while in some other reviews the set timeline have been adjusted severally (Cordell et al., 2009b). The 'peak phosphorus' period referred to a point when maximum production is reached and afterwards, a steady decline in production would occur even with increasing demand. The main challenge is that phosphorus deposits are not evenly distributed around the world. Phosphorus is concentrated only in few countries such as China, Morocco, Russia and the United States and collectively accounts for 70% of the global phosphate deposit (USGS, 2009).

Figure 1-1 shows the countries where phosphate rock was mainly sourced in year 2012. Among other countries, phosphate rock mining activities was highest in China followed by USA and Morocco. **Table 1-1** shows the uneven distribution of this resource in the world with largest deposits in Morocco and Western Sahara (50 million tonnes) followed by China (3.7 million tonnes) and Algeria (2.2 million tonnes). It also shows phosphate rock production in various countries in year 2013 (225 thousand metric tonnes) and 2014 (220 thousand metric tonnes) respectively which was projected to increase to 258 thousand metric tonnes in year 2018 (USGS, 2015). This increase will likely occur as a result of the expansion of existing phosphate rock processing plants in Morocco, Jordan, Russia, Peru, Tunisia and Kazakhstan in addition to the construction of new ones emerging in Saudi Arabia, China, Algeria, Egypt and Lebanon with the increased demand (Haneklaus et al., 2015). Today about 85-90% of the global mined phosphate rock (160 million tons per year) is used to meet global agricultural needs (USGS, 2014), some is diverted for animal feed while the majority is used for fertiliser production (Prud'homme, 2010; Hilton et al., 2010;Van Kauwenbergh, 2010).

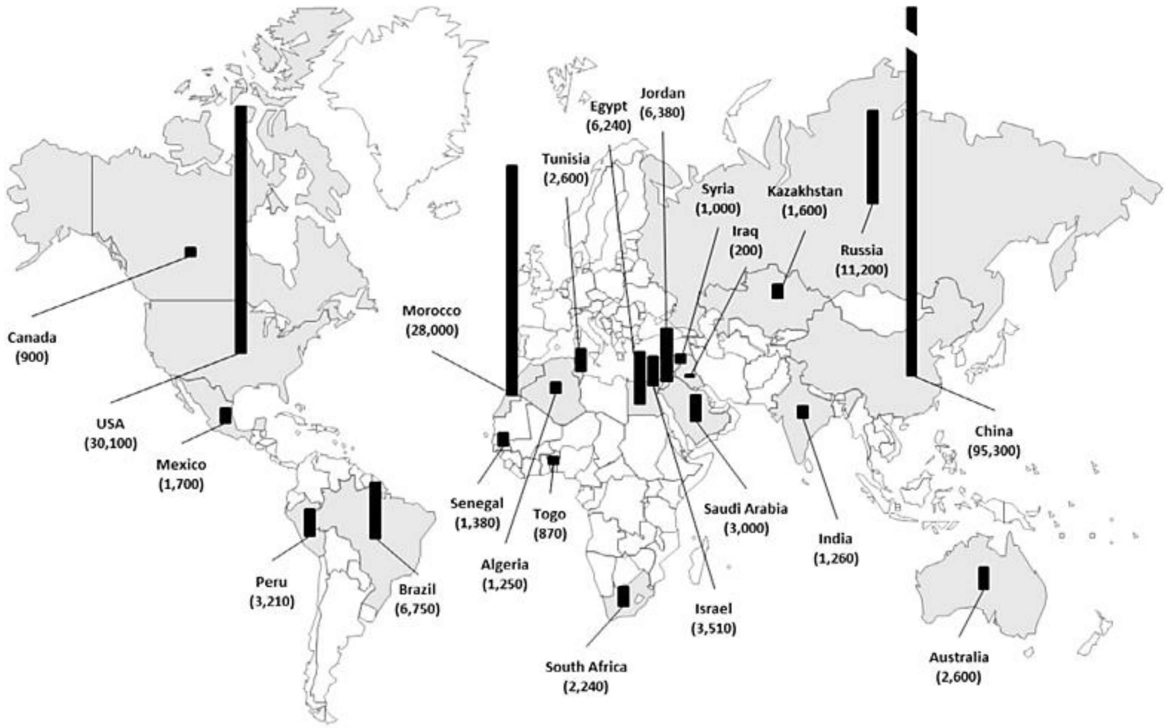


Figure 1-1: Mined phosphate rock (million tonnes) in various countries in year 2012 (Haneklaus et al., 2015)

Table 1-1: World phosphate rock production and reserves (USGS, 2015)

	Mine production		Reserves
	2013	**2014**[*]	
United States	31,200	27,100	1,100,000
Algeria	1,500	1,500	2,200,000
Australia	2,600	2,600	1,030,000
Brazil	6,000	6,750	270,000
Canada	400	-	76,000
China	108,000	100,000	3,700,000
Egypt	6,500	6,000	715,000
India	1,270	2,100	35,000
Iraq	250	250	430,000
Israel	3,500	3,600	130,000
Jordan	5,400	6,000	1,300,000
Kazakhstan	1,600	1,600	260,000
Mexico	1,760	1,700	30,000
Morocco and Western Sahara	26,400	30,000	50,000,000
Peru	2,580	2,600	820,000
Russia	10,000	10,000	1,300,000
Saudi Arabia	3,000	3,000	211,000
Senegal	800	700	50,000
South Africa	2,300	2,200	1,500,000
Syria	500	1,000	1,800,000
Togo	1,110	1,200	30,000
Tunisia	3,500	5,000	100,000
Vietnam	2,370	2,400	30,000
Other Countries	2,580	2,600	300,000
World total (rounded)	**225,000**	**220,000**	**67,000,000**

∗Estimated

Another main problem in addition to the limited resources, increase in phosphate rock prices and increasing demand, is the huge amount of energy involved in fertiliser production. Generally fertiliser production consumes large amount of fossil fuel energy and accounts for a third of the energy consumption used in crop production in the US (Gellings and Parmenter, 2004).

During the production of phosphate fertiliser, energy is used while burning sulphur to make sulphuric acid. This acid is then used for the dissolution of phosphate rock via the 'wet' process and produces phosphoric acid which is the basic ingredient used in production of phosphate fertilizers. Treatment and proper disposal of the generated waste product involves energy as well (Haneklaus et al., 2015). Although sulphur could be mined, most of the sulphur used in production is supplied by the oil and gas industry which generates large quantities of sulphur during the refining process (Dawson and Hilton, 2011).

During the production of most ammoniacal fertilisers, production of ammonium which is the basic ingredient via the Haber-Bosch process under optimal conditions consumes about 29 GJ t^{-1} (Fertilizers Europe, 2004; European Commission, 2006). The conversion of highly inert nitrogen gas (N_2) obtained from air to highly reactive ammonia (NH_3) is an energy intensive process. The Haber-Bosch process relies mainly on the supply of natural gas (CH_4) for process energy and also hydrogen gas (H_2) (Smil, 2001). Types of ammoniacal fertilisers include urea $CO(NH_2)_2$, ammonium phosphate, ammonium nitrate NH_4NO_3 etc with nitrogen usually expressed as a percentage of the total elemental nitrogen.

Even though fossil fuel such as petroleum, coal and natural gas are the main sources of thermal and electrical energy used in production lines and other production processes (Nunes et al., 2015), they still dominate the energy market and are likely to remain the major energy sources until year 2030. Therefore their use in the fertiliser industry is still a major drawback as they are non-renewable forms of energy which emit greenhouse gases (GHG) on combustion into the atmosphere causing global warming and climate change (Shafiee and Topal, 2009). About 60% of the total energy generated are greenhouse gases which include CO_2, methane, nitrous oxide, sulfur hexafluoride, HFCs and PFCs (Nunes et al., 2015; Hua et al., 2016). Global greenhouse gas emissions are generated during fertiliser production (0.93%), fertiliser distribution (0.07%) and fertiliser use (1.5%) (International Fertilizer Industry Association, 2009). In addition to global warming and climate change, fossil fuels are also responsible for environmental damage and health concerns (Pittman et al., 2011). However with energy emission constraints and high cost of fossil fuels, there is need to implement energy efficiency measures during production and use of fertilisers.

The aforementioned limitations facing the fertiliser industry emphasizes the need for sustainable food production. The increasing demand to reduce dependence on the use of fossil fuel energy and especially the uncertainties regarding the availability of resources have been the main drivers towards valorising and recovering nutrients from biomass (Leogrande et al., 2013;Vaneeckhaute et al., 2013). An important challenge in the transition from a fossil fuel economy to a bio-based economy is recuperation and recycling of valuable nutrients from waste streams in a sustainable but environmentally friendly manner (Vaneeckhaute et al., 2013). The concept of a bio-based/circular economy is aimed at using resources in a more sustainable way, reducing the use of resources, reducing waste and enhancing recycling and re-use which will be beneficial to both the environment and the economy (European Commission, 2015). With the uncertainties pertaining to resource availability, the nutrients present in waste could be recovered/recycled as fertilisers.

Waste streams such as food wastes, manures, sewage sludge and digestate from anaerobic digestion have gained research interests as potential renewable sources of recoverable plant nutrients and are often regarded as major pathways of phosphorus loss in the environment (Azuara et al., 2013). These wastes are not only generated in enormous quantities, but have characteristic high moisture content resulting in high degradation rate which presents increased concerns regarding their proper management and safe disposal. In wastewater treatment plants, phosphorus is regarded as a pollutant whereas it is a resource in fertiliser production. Wastewater is one of the most concentrated and partly unexploited phosphorus streams for nutrient recovery and recycling (Hukari et al., 2016).

Traditional management of these kind of wastes involves application to land as fertiliser, incineration or landfilling. However as these wastes have unequal proportion of plant nutrients, and contain heavy metals as well as pathogens, excessive application on farmland to meet crop nutrient demand results in higher doses of nutrients and these contaminants in the soil (Szogi et al., 2015). More so, this practise is limited due to strict regulations on pathogen and heavy metal contamination during waste disposal (H. Wang et al., 2008). During rainfalls, these nutrients move, contaminating both surface and ground water and result into eutrophication and hypoxia (Liang et al., 2014). Due to the characteristic high moisture of these wastes, incineration can only be achieved with a dry material which requires lots of energy to evaporate the water (Vom Eyser et al., 2015). With the increasing pressure from the general public and regulators, landfilling is currently being phased out in many countries due to emission of methane on sites and secondary pollution from the emanating leachate (H. Wang et al., 2008).

1.2 Hydrothermal processing: A potential route for nutrient recovery

Hydrothermal processing is an emerging but promising technology which has been perceived as a cost-efficient and effective way to convert nutrient-rich wet wastes such as manures and bio-solids directly to energy with an added advantage for nutrient recovery. The aspect of nutrient recovery via hydrothermal processing aligns perfectly with the EU Waste Framework Directive which is the legislative scheme for collection, transportation, recovery and disposal of waste. This directive ensures that waste is either recovered or disposed without causing any negative impact of human health or the environment. **Figure 1-2** shows the waste hierarchy which lists the possible measures which could be applied to wastes in order of priority from the most preferred option to the least preferred option. It encourages first the prevention or reduction of waste generation and its harmfulness. Secondly, it encourages that waste be recycled, re-used or reclaimed by any other process with the aim to extract secondary raw materials or using waste for energy production. Extracting and recovering nutrients from these wet wastes is a way of recycling these nutrients into useful products for use as sustainable sources of fertiliser.

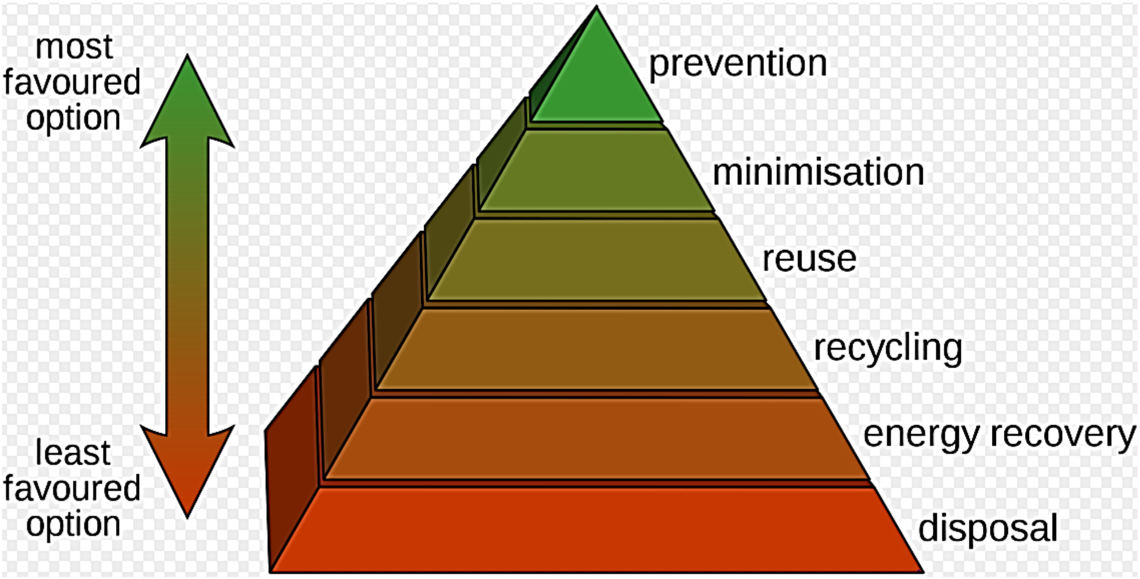


Figure 1-2: The waste hierarchy (DEFRA, 2013)

Hydrothermal processing involves treating biomass in water at elevated temperature and pressure sufficient to keep the water in the liquid state or in a subcritical state (Peterson et al., 2008). Hydrothermal processing facilitates the extraction of nutrients from these wastes which could be recycled for microalgae cultivation to produce more biomass for biodiesel (Biller et al., 2012;Heilmann et al., 2014) or can be recovered by other methods into usable forms. It produces a solid residue with immobilised phosphorus, making it less soluble compared to the untreated biomass and would not cause environmental pollution when applied to land.

The process is efficient as the cost of dewatering or drying as in the case of conventional waste treatment is avoided (Peterson et al., 2008). One of the unique features of this process is that it utilises water as a reactant which makes it suitable for wastes with very high moisture content. Furthermore, the process destroys pathogens, eliminates characteristic waste odour, reduces soluble toxic metals and ensures easy transportation of products (Qian and Jiang, 2014; Vom Eyser et al., 2015). In addition to these benefits, it can serve as a pre-treatment option for nutrient-rich wet wastes transforming them to valuable energy fuels in either solid, liquid or gaseous forms.

Hydrothermal processing temperatures could either be low or high. Low temperature processing includes thermal hydrolysis and hydrothermal carbonisation while high temperature processing is hydrothermal liquefaction and super-critical water gasification. Processing at lower temperatures up to 170^{o}C otherwise known as thermal hydrolysis (TH) generally results in hydrolysis of the carbohydrate fractions and extracts inorganics. It is often used as a pre-treatment at temperatures in the range 160-170°C prior to anaerobic digestion to enhanced biogas yields. Increasing the temperature and pressure further, results in the carbonisation of the residue, reducing its oxygen content and increasing its carbon content. The latter is termed hydrothermal carbonisation (HTC) and is under investigation to produce high energy density biofuels from wet wastes. Hydrothermal carbonisation (HTC) is operated at 180-250°C and pressure between 2 and 10 MPa, and produces a carbon-rich bio-coal with high energy content (Mumme et al., 2011). Only limited studies have focussed on hydrothermal carbonisation of manure to produce bioenergy (He et al., 2000; Heilmann et al., 2014). Hydrothermal liquefaction (HTL) is usually operated at 280-370°C and at pressures ranging from 10-25 MPa and produces a synthetic bio-crude with high energy content (Biller and Ross, 2011). Several studies have investigated the higher temperature processing of manure to produce bio-oils via hydrothermal liquefaction (Xiu et al., 2010; Vardon et al., 2011; Theegala and Midgett, 2012). Supercritical water gasification (SCWG) is operated at temperatures above 450°C and pressure above the critical point of water (22 MPa) producing high energy syngas containing H_2,CO_2 and CH_4 (Toor et al., 2011).

1.3 Novelty of research

Generally there has been extensive research on hydrothermal processing of wastes such as sewage sludge (Zhu et al., 2011;Xu et al., 2012) and to a lesser extent manures but most have focused on energy densification (He et al., 2001;Titirici et al., 2007;Funke and Ziegler, 2010;Berge et al., 2011;Theegala and Midgett, 2012;Chen et al., 2014). In the aspect of nutrient recycling, a number of studies have investigated the concentration of phosphorus in either the solid product or the aqueous product while a few considered nutrient recycling using aqueous waste streams from hydrothermal processing for biomass cultivation (Jena et al., 2011;Biller et al., 2012;Du et al., 2012;Cherad et al., 2013;Garcia Alba et al., 2013).

There has been no study which has previously compared the product yields and extraction of NPK from the same feedstock via all four hydrothermal processing routes using the same reactor conditions. Also there are no reports on the hydrothermal processing of swine manure in the presence of acid and alkali additives to explore the possibility of optimal nutrient extraction. Most of these studies have not reported the fate of nutrients during hydrothermal processing. As this will give an insight on the potential uses of products and possible routes to consider in order to recover vital nutrients like nitrogen and phosphorus. Although some of the studies investigated some metal species, there is no literature on metal distribution during low temperature hydrothermal processing.

This study investigates the product yields and fate of NPK in the process streams following thermal hydrolysis, HTC, HTL and SCWG of swine and chicken manure and compares this to digestate and microalgae. Also this study investigates the influence of additives (e.g., acid and alkali) on the hydrothermal treatment of swine manure. The influence of pH on the extraction of nitrogen and phosphorus is presented following mild hydrothermal treatment (i.e., thermal hydrolysis-TH) and more severe treatment (i.e., hydrothermal carbonisation-HTC). The distribution of metals during these processes were investigated. Finally, the potential of recovering both nitrogen as ammonium and phosphorus as phosphate from these aqueous waste streams was investigated.

1.4 Aim and objectives of Thesis

The aim of this research is to determine nutrient distribution during hydrothermal processing of waste biomass, enhance nutrient extraction and explore the potential to recover these nutrients by biological means or by physical recovery using modified biochar.

In order to achieve this aim a number of objectives have been outlined as follows:

1) To determine the product yields, nutrient and metal distribution by performing a scoping study on feedstock behaviour with microalgae – *C.vulgaris*, swine manure, chicken manure and digestate during low and high temperature hydrothermal processing under normal conditions with water.

2) To evaluate the effect of using mineral acid, alkali and organic acids on nutrient extraction into the aqueous product and metal distribution between products

during low-temperature hydrothermal processing (120°C-250°C, 60 minutes) of swine manure.

3) To evaluate nutrient and metal distribution during microwave pre-treatment of various wet biomass such as microalgae, swine manure, chicken manure, digestate and sewage sludge under normal conditions with water.

4) To evaluate the effect of using mineral acid, alkali and organic acids on nutrient extraction into the aqueous product and metal distribution during low-temperature microwave pre-treatment (120°C, 15 minutes) of swine manure.

5) To compare nutrient extraction from swine manure using microwave heating (120°C, 15 minutes) and conventional heating (120°C, 60 minutes) under normal conditions with water, mineral acid, alkali and organic acids.

6) To investigate the potential of recovering nutrients present in aqueous products from SCWG of *C.vulgaris*, sewage sludge and various seaweeds-*L.digitata*, *Saccharina* and *Alaria* esculenta using a freshwater microalgae-*C.vulgaris* by monitoring its growth rate, biomass concentration and volatile content.

7) To determine the maximum concentration and suitable working pH required for high phosphate adsorption efficiency from hydrothermal aqueous products using a modified oak-derived biochar.

1.5 Thesis outline

This thesis has been divided into separate chapters according to the objectives outlined above and illustrated in **Figure 1-3**.

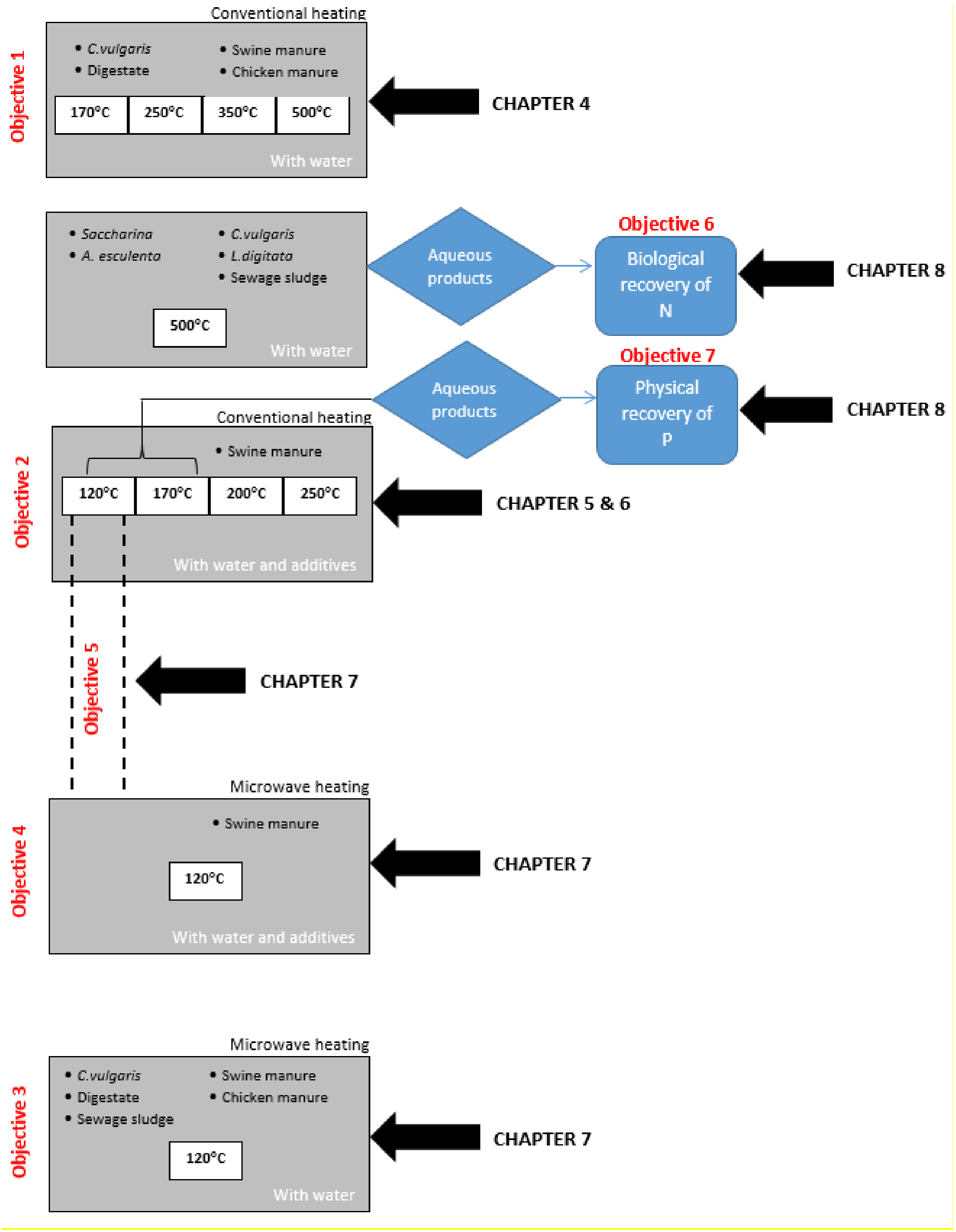


Figure 1-3: Overview of research objectives and the link to thesis chapters

Chapter 1- "**Introduction**": This chapter reviews the various challenges facing the fertiliser industry such as limited resources, increasing demand and the need for sustainable food production. It identifies the energy intensive processes involved in fertiliser production and the increased dependence on fossil fuels which emit greenhouse gases on combustion. Finally it addresses recycling and recovery of nutrients from wet waste via hydrothermal processing as they tend to cause environmental pollution when not treated or disposed properly.

Chapter 2- "**Literature review**": This chapter gives a more detailed information on the composition of waste biomass, current waste management practices, review of literature on studies done on other waste to energy technologies, review of literature on various studies performed on hydrothermal processing in aspects such as product yields, nutrients, energy and metals, review of literature on general approaches on phosphorus recovery and recovery through hydrothermal processing, review of literature on other phosphorus recovery methods.

Chapter 3- "**Materials and Methods":** This chapter presents in detail the origin and type of biomass investigated, sample preparation, analytical methods employed in feedstock characterisation, experimental setup of hydrothermal processes investigated, the process conditions such as temperature, pressure and reagents used. It also contains detailed information on product recovery methods employed and product analytical methods. In addition it contains experimental setup for both biological and physical nutrient recovery.

Chapter 4- "**Comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing**": This chapter is primarily focused on objective 1. It presents the results of product yields, characterisation of aqueous and solid products for metals and nutrients, forms of extracted nutrients in aqueous product and nutrient extraction. The general trends observed are discussed with literature.

Chapter 5- "**Influence of pH on hydrothermal treatment of swine manure: Impact on extraction of nitrogen and phosphorus**": This chapter is primarily focused on objective 2. It presents the results of product yields, characterisation of aqueous and solid products for nitrogen and phosphorus, nutrient extraction, forms of these extracted nutrients in aqueous product, mass balance of nutrients between products. The general trends observed are discussed with literature.

Chapter 6- “**Influence of pH on hydrothermal treatment of swine manure: Impact on metals**”: This chapter is primarily focused on objective 2. It presents the results of product yields, energy content of recovered solid products, influence on ash and metal content of the solid products, mass balance of metals between products. The general trends are discussed with literature.

Chapter 7- “**A comparison of nutrient extraction using microwave and conventional heating during thermal hydrolysis**”: This chapter focuses on objectives 3, 4 and 5. It presents the results of product yields, characterisation of aqueous and solid products for nitrogen and phosphorus, nutrient extraction, forms of these extracted nutrients in aqueous product, mass balance of nutrients between products. The general trends observed are discussed with literature. In addition, it compares extraction of nitrogen and phosphorus using microwave heating and conventional heating.

Chapter 8- “**Recovery of nutrients from hydrothermal aqueous waste streams**”: This chapter is primarily focussed on objectives 6 and 7. It contains composition of SCWG aqueous products used for biological recovery of nutrients with microalgae, growth curves, growth kinetics and biomass and volatile suspended concentration. In addition, it contains results obtained during phosphate adsorption with modified biochar as well as SEM images and EDX composition of adsorbed biochars.

Chapter 9- “**Conclusion and future recommendation**”: This chapter discusses the main conclusions from these objectives, significance of this research on an industrial scale and future recommendations.

Chapter 2 Literature Review

2.1 Biomass

Biomass has been considered to be one of the most promising sources of renewable energy as it is an alternative to the conventional energy and has potential for use in many countries (Ozcan et al., 2015). It contributes about 14% of the world annual energy consumption (Shen et al., 2009).

Biomass is generally considered to be a low status fuel which offers diverse range of fuels in either solid, liquid or gaseous state using various conversion technologies (Ozcan et al., 2015). Currently there is a wide range of biomass to energy projects across various countries (Ozcan et al., 2015). Among the alternative sources for energy, biomass has been shown to be the most viable option to address the energy shortage and environmental concerns which is one of the problems associated with the use of fossil fuels. Biomass refers to any matter of biological origin such as plants, terrestrial or aquatic animals (Demirbas, 2001). Materials such as wood, crop residues, algae, agricultural waste, municipal solid waste, animal waste are all generally referred to as biomass. They are a major source of natural fibres, novel materials and organic chemicals (Demirbas, 2004). Most of the energy used before the advent of coal, natural gas and petroleum were from wood which has energy stored from the sun during photosynthesis and on combustion, they produce less CO_2 – a greenhouse gas compared to fossil fuels which is easily assimilated by plants for photosynthesis over a short cycle (Demirbas, 2001).

2.2 Types of wet biomass

2.2.1 Livestock manure

In the past, swine production was practised on a small scale usually owned by individuals who recycled manure on land as fertiliser. Nowadays there has been major structural changes in the industry. There has been extensive changes in swine production in recent years with increasing numbers of swine confined to a small land area. In the past decades, consolidation of animal feeding operations into fewer but larger scale operations has increased in many nations such as Mexico, Netherlands, Denmark, France, United States (Brands, 2014). As a result of the extensive growth in concentrated animal feeding operations in the past decade, huge amounts of manure are generated leaving farmers with the challenge of proper waste disposal (Szogi et al., 2015). As stated in the FAO, (2007) report, over 23 million tons per day of cattle manure was produced globally. About 8.4% of the total animal weight is excreted daily as raw manure-urine and faeces (Hatfield et al., 1990).

Traditionally, manure is applied to land close to the production areas, however they are now considered as sources of environmental pollution and potential sources of air pollution, surface and ground water (Burton and Turner, 2003). Disposal of animal manure is one of the problems associated with establishing or expanding concentrated animal feeding operations. Another problem is that the confinement facilities and storage facilities emit odorous and volatile compounds such as hydrogen sulphide (H_2S), ammonia (NH_3), aldehydes, alcohols, ketones, amines, amides, phenols, alkenes, esters and greenhouse gases (CO_2, CH_4, N_2O, etc.) which have resulted in public complaints from inhalation and associated health problems (Hatfield et al., 1990; (Schiffman et al., 2001;Yang et al., 2014). This has led to increased awareness by regulatory bodies and the general public on the issues of soil, water and air pollution around swine production facilities (Schiffman et al., 2005). Therefore livestock producers are concerned about developing new methods and technologies to meet regulatory requirements and maintain good environmental standards. For instance, strategies for ammonia reduction includes renovation of barns, change in animal nutrition, regular cleaning of exhaust air from farm structures and proper manure treatment (Ndegwa et al., 2008).

Swine manure is collected as either solid, semi-solid (slurry) or liquid form, depending on the facilities and manure collection system installed (Hatfield et al., 1990). Many swine production units digest liquid manure in anaerobic lagoons which volatilize about 70-90% of nitrogen present, converting it to ammonia which is lost in the atmosphere. As land is limited, this practise decreases the quantity applied to land by 10% (Hatfield et al., 1990).

Animal agriculture is undoubtedly of great importance to food production and improvement of many economies. However this practise should be balanced with sustainable manure management to prevent environmental degradation, improve agricultural benefits and reduce greenhouse gas emissions (Karakashev et al., 2008; Brands, 2014). Anaerobic digestion has been widely used locally in both small and large scale farms to generate biogas to be used for heat and power as well as for manure stabilization and odour control (Otero et al., 2011; Fernandez-lopez et al., 2015). Other strategies employed include phosphorus immobilization using alum to prevent runoff (Sharpley et al., 2007), energy generation either by combustion, gasification or anaerobic digestion or transportation of manure to P-deficient agricultural lands (Kelleher et al., 2002).

2.2.1.1 Composition of manure

Animal manure accounts for about 8% of the animal weight per day with very high moisture content of about 88% (Theegala and Midgett, 2012). The composition of manure, volatile emissions and nutrient released in manure is greatly determined by the dietary input (Miller and Varel, 2003). Manures generally contain high levels of organic matter which is responsible for its characteristic odour, pathogens, hormones, pharmaceutic derived compounds and vital plant nutrients such as nitrogen (N), phosphorus (P) and potassium (K). Nitrogen is most likely to be significantly reduced during manure handling and storage, but not P and K (Hatfield et al., 1990).

In addition manure also contain metals which are from their enriched diet. For instance the swine diet is usually prepared with corn, soybean or sorghum meal fortified with vitamins and minerals to prevent deficiency. About 50-100ppm of zinc is added to 5-10mgkg-1 of Copper, 0.3mgkg-1 of selenium, calcium and phosphorus (NRC, 1988). However a significant amount of these mineral content are excreted- 86% Cu, 100% Zn, 79% Mn, 40% Ca, 74% Mg, 59% K, 66% Na (Hatfield et al., 1990). Also about 85% of nitrogen present in a typical soybean or corn diet is digested. In the study by van Kempen et al., (2003), they found that swines retain about 50% of nitrogen, phosphorus and sulphur in their diet indicating that excess nutrients are excreted. It has been reported that a reduction in dietary protein and substitution with crystalline amino acids has a huge impact on excreted nitrogen (Kerr et al., 2006). Other studies indicate that about 40 - 60% of the phosphorus intake is digested although undigested phosphorus from cereal grains or other complexes can be excreted as phytic acid (NRC, 1988; Hatfield et al., 1990).

Although phosphorus accumulates in manure, the quantity and form in which it exists in animal manure depends on the age, class, nutrient content of the animal feed, added inorganic phosphorus supplements and the nutrient status of the pig (NRC, 1988). According to Havlin et al., (1999), fresh swine manure contains about 30 - 40% organic -P and 60 - 70% total inorganic –P. Nitrogen present in a typical soybean and corn diet is mainly excreted by pigs as uric acid in urine and organic-N in faeces (Hatfield et al., 1990). The disparities in the composition of manure is mainly attributed to the mode of collection, extent of dilution and storage but not dependent on diet (Hatfield et al., 1990).

2.2.1.2 Problems with land application of manure

As huge quantities of manure is generated from concentrated animal feeding operations (CAFOs), the farmers are faced with the problem of storage as well as safe and effective disposal of this waste (Szogi et al., 2015). Phosphorus is highly soluble and consequently lost to the environment when manure is applied on agricultural land (Liang et al., 2014). About 50% of inorganic phosphorus present in dairy manure is water soluble while about 95% of the soluble phosphorus leaches during rainfall (McDowell et al., 2001). In order to curtail phosphorus loss to the environment, there are strict legislations to be adhered to by farmers which require sustainable manure treatment/techniques to be established. Techniques such as mineral amendment using chemicals containing calcium or aluminium to immobilize this nutrient in manure have been developed (Wilson et al., 2008; Armstrong et al., 2012)

The nitrogen and phosphorus contents in pig manure and harvested crops are not proportional. The ratio of nitrogen and phosphorus in most grains and hay crops is 8:1 while in animal manure the ratio is much smaller at about < 4:1 (Zhang et al., 2002). So by directly applying manure to land repeatedly in order to attain optimal nitrogen rates needed for increased crop growth, excess phosphorus accumulates in the soil (Szogi et al., 2015). As a result of this imbalance, excess phosphorus in the soil is lost during rainfall through runoffs and leaching into nearby lakes and rivers causing accelerated eutrophication (Vitousek et al., 2009). To reduce this negative impact of phosphorus on the environment, phosphorus needs to be transported from the pig farm to phosphorus-deficient farmlands (NRCS, 2003). However it becomes less cost and energy effective when bulk manure is transported over a long distance from the site of manure generation (Keplinger and Hauck, 2006).

2.2.1.3 Manure Management

Manure management in concentrated livestock regions should ideally include new technologies to recover phosphorus in a concentrated but usable form instead of applying directly on farmlands. Using this approach, transportation of manure over a long distance is avoided, with a huge reduction in agronomic imbalance or loss of phosphorus to water resources (Szogi et al., 2015). In the past decades, there has been enormous consolidation of confined animal feeding operations (CAFOs) resulting in the need for new state-of-the-art waste management facilities on site for economical viability and environmental reasons (Cantrell et al., 2008). Also the rising energy prices, increased demand for energy supplies and the potential environmental threat of traditional waste management systems are factors which have driven the need for on-site waste to bioenergy facilities (Mcnab et al., 2007). Biofuel production on a farm scale will provide an opportunity for the agricultural sector to improve the soil, water and air quality while reducing their dependence on imported fossil fuels (Muller et al., 2007). The use of animal manure and other on-site organic products as bioenergy feedstocks would allow farmers to explore new market for traditional waste products. This would generate annual revenues and diversify farm income (Cantrell et al., 2008).

2.2.2 Sewage sludge – A product of the wastewater treatment plant

In a wastewater treatment plant, solids present in the influent wastewater are separated, dewatered and treated appropriately in order to meet the acceptable requirement for pollutant and pathogen levels as enforced by the local environmental protection agencies. The treatment process is shown in **Figure 2-1** and involves the preliminary, primary, secondary and tertiary stages. The aim of every wastewater treatment process is to remove suspended solids, eliminate biochemical oxygen demand (BOD), coliform bacteria, toxic compounds as well as nutrients such as NO_3^- -N, NO_2^- -N, NH_4^+-N, PO_4^{3-}P (Abdel-Raouf et al., 2012). Large materials such as wood, rags, heavy grit particles and faecal matter are removed in the preliminary stage through a 20-60mm screen leaving organic matter suspended. The effluent then goes on to the primary stage which removes 70% of the settleable solids by gravity and about 40% of BOD (Horan, 1990). The effluent then flows into the secondary stage which is designed to remove BOD from organic matter using mixed heterotrophic bacteria which utilize organic matter for their growth and energy. This produces activated sludge. Finally the tertiary stage removes all organic ions either by biological means or chemical means (Abdel-Raouf et al., 2012).

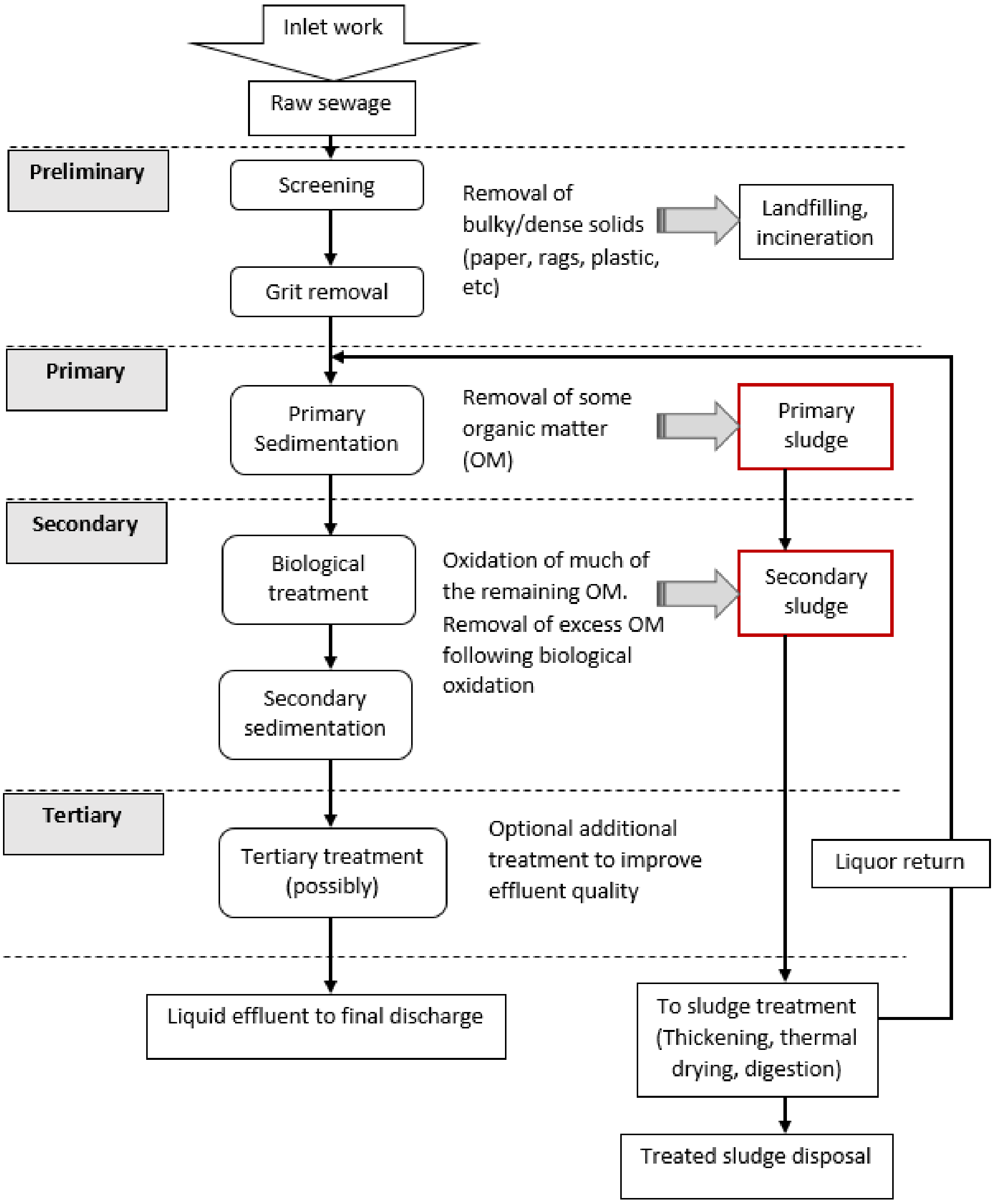


Figure 2-1: Typical stages in conventional wastewater treatment works (Adapted from Tchobanoglous et al., 2003)

2.2.2.1 Composition of sewage sludge

Sewage sludge contains valuable nutrients such as nitrogen and about 1-10% phosphorus which serves as an important source of phosphorus recovery in the ecosystem (Zhu et al., 2011;Manara and Zabaniotou, 2012;Qian and Jiang, 2014). It contains other components with agricultural value to a lesser extent are K, Ca, Mg and S while inorganics such as aluminates and silicates are also present. In dry form, it has a high calorific value which is similar to fossil coals (Horan, 1996). It is mainly composed of moisture, about 60% non-toxic organic matter on dry basis, typical ash content of about 35%, significant quantities of free lipids (mono-, di- and triglycerides, fatty acids and phospholipids) and high pathogenic microbial load (Melero et al., 2015;Yu et al., 2015). The microorganisms present in the sludge are also a source of lipids since they have lipid rich cell membranes which includes steroids, phospholipids, fatty acids having C_{10}-C_{18} (Melero et al., 2015). Compounds such as hydrocarbons, tocopherols, sterols and carotenes are also present in sewage sludge (Siddiquee and Rohani, 2011). As municipal waste water originates from various sources, sewage to a large extent contains undesirable pollutants such as Hg, Cd, Cr, Ni, Cu, Pb, Zn, As in concentrations ranging from less than 1ppm to 1000ppm (Manara and Zabaniotou, 2012;Zhao et al., 2014b).

2.2.2.2 Disposal of sewage sludge

Treatment of municipal wastewater results in the generation of huge amounts of sewage sludge mainly from the primary and secondary stages and needs to be managed in an environmentally acceptable way before final disposal. However the management of sewage sludge is difficult and expensive in many countries (Qian and Jiang, 2014). For instance in 2010, about 20.76 million tons of sewage sludge containing up to 80% moisture was produced in China and it is expected to be much higher at the end of 2015 (Zhao et al., 2013; Zhao et al., 2014b). As it is not feasible to reduce the amount of municipal wastewater going to wastewater treatment plants due to the rate of population growth, urbanization and industrialization, it is believed that the generation of sewage sludge would gradually increase in the coming decades (Zhao et al., 2014b). Therefore the management of sewage sludge will continue to be a major concern requiring an appropriate solution.

Only a limited amount of sludge is needed on agricultural land and most of it (70%) is disposed of in landfills (Fytili and Zabaniotou, 2008). The report from the US Environmental Protection Agency (US EPA, 1999) indicated that about 60% of sewage sludge were applied to land while 40% was either incinerated, landfilled or disposed by any other means. In Germany, the government banned the disposal of sewage sludge by any other means except incineration or use in agriculture (Vom Eyser et al., 2015). Although the aim of applying sewage sludge on land is to recycle nutrients such as phosphorus and nitrogen, there is still a potential risk associated with inherent contaminants. Application of sewage sludge on land as with the case in manure has raised concerns from the public due to generated odour and the perceived risk this may cause to the people. In many countries, the use of sludge for the production of fertilisers and compost is restricted due to the presence of metals (Siddiquee and Rohani, 2011) and residual pharmaceutical compounds (Kamler and Soria, 2012). More so, nowadays the cost of landfilling is increasing and unfavourable, making these two traditional disposal methods less ideal for such waste (Fytili and Zabaniotou, 2008; Fonts et al., 2012). Thermal treatment of sludge either by incineration, wet oxidation, pyrolysis and gasification is a more sustainable approach towards sludge disposal, reducing sludge volume significantly and increases energy content as well. For instance the by-products incineration ash and biochar from pyrolysis could be used as construction materials, soil conditioners and fertilisers (Hossain et al., 2011; Qian and Jiang, 2014).

2.2.3 Algae

Interest in algal biomass as a source of third generation biofuels has received increased attention in the last few years due to climate change concerns and increasing energy demand from a growing world population (Lopez Barreiro et al., 2014).

The benefits being that algal biomass grows quickly, requires small land area unlike terrestrial biomass and could be cultivated in such a way as to increase their lipid content with varying compositions (Lu and Savage, 2015). In addition, owing to the large amounts of wastewater generated from domestic and industrial sources, algae could be cultivated to utilise the organic nutrients present in waste streams instead of discharging them into the environment causing pollution and health risks (Brennan and

Owende, 2010;Rawat et al., 2011). This offers an added advantage of reduced wastewater treatment cost as research has shown that algae take up these nutrients to form biomass and significant amounts of lipid content leaving the water treated (Wang et al., 2010). Several papers have highlighted the merits and demerits of using algal biomass for biofuel (Patil et al., 2008; Khoo et al., 2013; Liu et al., 2013) while several techniques for the conversion of algal biomass to biofuel were discussed in detail by Brennan and Owende, (2010).

2.2.3.1 Composition of algal biomass

Many microalgae species have a large build-up of lipids which are stored in their various cell membranes, the quantities obtained in dry biomass weight differ between species (Mata et al., 2010). However, this can greatly increase as a result of environmental stress such as high salinity, nutritional deficiency and cultivation conditions (Dunahay et al., 1996;Takagi et al., 2006;Mata et al., 2010). **Table 2-1** compares the potential oil yield and land requirement of microalgae biomass per hectare compared to the other biomass feedstock. It shows the similarity between the oil contents in both microalgae and seed plants, but clearly states the advantage of microalgae having high biodiesel productivity and the least land requirement.

Interest in algae biodiesel has also led to an extensive study on lipid extraction from algae (Mata et al., 2010) and the performance of lipid-extracted algae during HTL (Vardon et al., 2012). These lipids could be used in the production of chemicals or omega 3 fatty acids for food (Vanthoor-Koopmans et al., 2013). Other studies on protein extraction are Huo et al., (2011) and Garcia-Moscoso et al., (2013) which could be used in the production of antioxidants for human and animal nutrition and fertilisers for plant nutrition (Vanthoor-Koopmans et al., 2013).

Table 2-1: Potential Oil Yield and Land Use of Microalgae Compared to Other Biomass Feedstock (Mata et al., 2010)

Biomass	Oil Content (% of dry weight)	Oil yield (Litres/hectare)	Land Use (m^2year/kg biodiesel)
Corn	44	172	66
Hemp	33	363	31
Soybean	18	636	18
Jatropha	28	741	15
Camelina	42	915	12
Rapeseed	41	974	12
Sunflower	40	1070	11
Castor	48	1307	9
Palm oil	36	5366	2
Microalgae (low-lipid)	30	58,700	0.2
Microalgae (medium-lipid)	50	97,800	0.1
Microalgae (high-lipid)	70	136,900	0.1

2.2.3.2 Growth requirements for microalgae

Microalgae can either grow heterotrophically, autotrophically or mixotrophically (Graham et al., 2009). Photosynthetic microalgae otherwise known as autotrophs require inorganic compounds such as salts, CO_2 and light for growth as shown in **Figure 2-2**. One of the key characteristic of these organisms is their ability to produce large amounts of biomass through photosynthesis in a similar way as plants when cultivated (Mata et al., 2010). They can complete their entire growth cycle in days unlike the terrestrial energy crops which have longer growing seasons (Feng et al., 2011). Photosynthesis is a process in which autotrophs trap solar energy with the help of chlorophyll pigments to utilise CO_2 into carbohydrates which is an energy rich organic compound as well as proteins and lipids (Demirbas, 2001;Jorquera et al., 2010). This solar energy is stored as chemical energy in the form of carbohydrates and oxygen is released as indicated in the equation below (Ross, 2011).

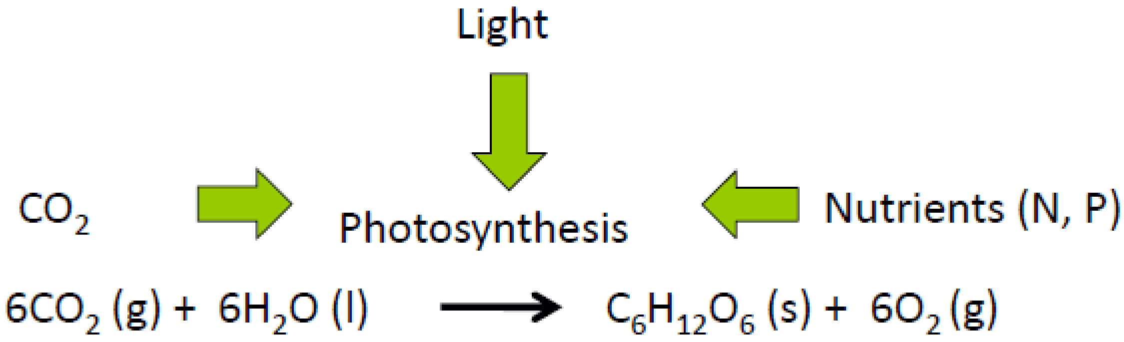


Figure 2-2: Requirements for photosynthetic algae growth (Ross, 2011)

2.3 Modern technologies Waste to Energy conversion processes

Unlike traditional waste management practices, conversion of organic biomass exists on two basic platforms – the biological / biochemical platform and the thermochemical platform. There are treatment processes within these platforms primarily designed to eliminate odour problems, reduce pollution potential, reduce volume, recover energy as well as recover inherent nutrients (Cantrell et al., 2008). Selection of a conversion process usually depends on important factors such as the economics, quantity of biomass or feedstock available and its characteristics. However in most cases, the desired energy of the final product overrides all other factors (McKendry, 2002a;McKendry, 2002b).

2.4 Biochemical conversion processes

This involves the use of living organisms or their products in the conversion of organic material to fuels (US Department of Energy, 2002). Conversion of these materials is achieved by both anaerobic and photosynthetic microorganisms, producing gas and liquid fuels. Most times, the solid by-product is rich in nutrients and could be an alternative source of fertlizer. Biological processes require longer reaction times ranging from a few days to weeks and at times even months (Cantrell et al., 2008). Examples of biochemical conversion processes are anaerobic digestion and bio-hydrogen production.

2.4.1 Anaerobic digestion (AD)

Anaerobic digestion has been considered to be an environmentally friendly approach with a reduction in gas emissions. Anaerobic digestion has gained increased interest over the years especially in the aspect of manure stabilization, pathogen reduction, odour control, sludge reduction and energy generation. Therefore it is an integral part of a modern wastewater treatment plant. Anaerobic digestion has been widely used in treating different types of wastewater from petrochemical industry, palm oil mill, distillery, olive oil mill, piggery, dairy, fishery and municipal areas before discharging effluent and also for energy generation (Li et al., 2014; Zhang et al., 2014).

It involves breaking down complex organic wastes by a community of anaerobic microorganisms, producing biogas which is mainly composed of methane (CH_4) and carbon dioxide (CO_2). The process is categorized into three main stages – hydrolysis, fermentation and methanogenesis. AD reduces sludge volume to about 40% (Perez-Elvira et al., 2011). Approximately 50–70% organic matter is readily decomposed leaving residual organic matter which forms the digestate as shown in **Figure 2-3** (Zhang et al., 2007).

During the hydrolysis stage, complex molecules are broken down into soluble compounds, making it available for the fermentative bacteria (acidogenic and acetogenic bacteria). These bacteria convert the soluble components into acetic acid, alcohols, volatile fatty acids and gases containing H_2 and CO_2 while the methanogens convert the intermediate products into CH_4, CO_2 and other gases (Cantrell et al., 2008). **Figure 2-3** shows the end products of the anaerobic digestion process and their potential application. After digestion, the digestate is separated in a solid-liquid separator and the liquid fraction could be used as fertiliser since it is rich in ammonium while the solid fraction is stabilized as compost and used as a soil amendment (Ledda et al., 2013; Monlau et al., 2016). The biogas produced could be combusted in a heater, boiler or engine and used on farms to meet its heating needs. Electricity can also be generated from the biogas as well and excess could be sold to a local utility company (Cantrell et al., 2008).

Installation of anaerobic digesters require a high initial capital investment with subsequent high standards of maintenance and management, have low organic degradation efficiency of about 30-50% in mesophilic AD, long retention times, restricted production of methane (Strong et al., 2011). Several research studies have attributed this low performance to the hydrolysis step of components in the biomass such as flocs, microflocs, cellulose, lignin, hemicellulose, lipids and proteins (Carballa et al., 2011). Therefore the major concern is to improve the methane yield from the mesophilic stage and improve the degradation efficiency of the dry organic solids (Abelleira-Pereira et al., 2015). Feedstocks like manures with high nitrogen require co-digestion with cheap high carbon co-substrates (e.g. agricultural residues) in order to avoid microbial inhibition (Moller et al., 2004;Jiménez et al., 2015). In Europe, co-digestion is being practised even on an industrial scale using different waste streams to help improve substrate deficiencies, nutrient balance, methane yields (Chowdhury et al., 2014; Ye et al., 2014;Jiménez et al., 2015). Digestate recovered from this process is a biologically stable product high in nutrients such as nitrogen and phosphorus with significant organic fraction (Tambone et al., 2010; Ledda et al., 2013).

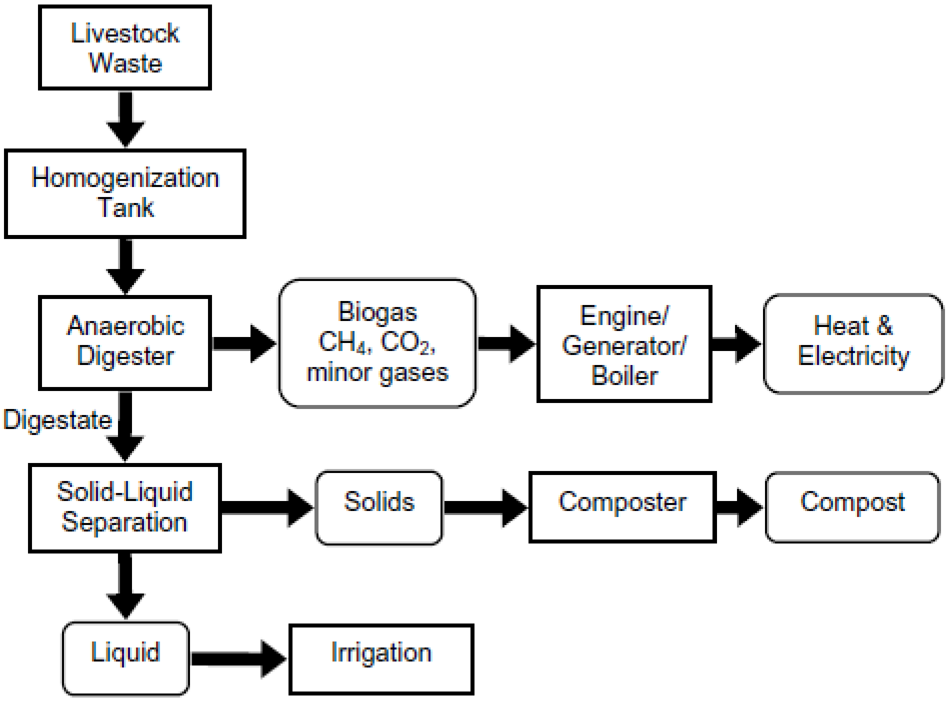


Figure 2-3: The anaerobic process showing end point of products (Cantrell et al., 2008)

2.4.2 Bio-hydrogen production

Hydrogen gas has been predicted by experts as the next generation of energy and capable of replacing fossil fuels (Hoffmann, 2001). Hydrogen is green in nature and when combusted it forms water. Biological production of hydrogen from biosolids is an emerging technology unlike the anaerobic digestion process which has been widely established. The process is divided into three; a two-stage photosynthesis and H_2 production by algae, photobiological process by photo-fermentative bacteria and fermentation process (dark fermentation) by anaerobic fermentative bacteria (Cantrell et al., 2008). Hydrogen has been produced from waste materials (Angenent et al., 2004; Kapdan and Kargi, 2006; Li and Fang, 2007). However these reviews identified that waste rich in carbohydrates are the most suitable and untreated biosolids such as animal waste is not ideal for the process.

2.5 Thermochemical conversion

The conversion efficiency of any thermochemical process is significantly affected by the feedstock characteristics (Cantrell et al., 2007). The most important parameter being the total solids, volatile solids and ash contents. The total solids determines the type of conversion process which will be suitable as well as the necessary pre-treatment method/dewatering technique to use. The volatile solid gives an insight on how easily a feedstock could be utilized as an energy source while the ash content is the non-degradable fraction of the feedstock which includes alkali metals such as K, Na, Ca and Mg. Feedlot manure or poultry manure are often collected along with a mixture of bedding and waste feed and sometimes with underlying soil making it generally dry. The presence of soil in the mixture increases the ash content, but decreases both the carbon content and volatile solids and consequently affects the higher heating value (HHV) of this feedstock. Collection from swine and dairy feeding operations are usually dilute containing a mixture of wash water, urine, manure and undigested feed (Cantrell et al., 2007). Significant amount of volatile solids (between 69-84%) is usually present in dairy and swine manure as they contain more organic matter than either poultry or cattle manures.

2.5.1 Conventional thermal treatment

This involves physical breakdown of the bonds present in organic matter using high temperature reforming the intermediates produced into hydrocarbon fuels, synthesis gas or residual charcoal (Cantrell et al., 2007). Thermochemical conversion can occur in seconds or minutes , reducing the footprint requirements and yielding several complex end-products (Bridgwater, 2006). Other advantages of these conversion are reduction in gas emissions, capable of handling a variety of feedstocks and blends, elimination of pathogens and pharmaceutical acive compounds as well as efficient nurient recovery (Cantrell et al., 2007). Also the quantity of residue generated is greatly reduced compared to the unprocessed feedstock. These processes include combustion, pyrolysis, liquefaction and gasificaton. Livestock manure has been used as a feedstock in some of these processes.

The end product usually depends on the operating temperature, pressure, residence time and heating rate and is a combination of solids, bio-oil and volatile gases (Bridgwater and Peacocke, 2000). These volatile gases are a combination of water vapour, CO_2, N_2, H_2, tars and hydrocarbons. Condensation of the tars produce bio-oil which is combustible source of fuel. The solid product (char) on the other hand contains minerals and fixed carbon. Thermochemical conversion integrated with biological processes could provide an additional pathway to valorising manures (Fernandez-lopez et al., 2015).

The synthesis gas from pyrolysis and gasification could be used as fuel gas when impurities such as dust, metals, organic acids, tars and water are removed (Cantrell et al., 2008).

2.5.1.1 Combustion

This converts biomass energy to heat which can not be stored. There are various contributing factors that affect the efficiency of biomass combustion. One is the heterogeneous nature which makes energy recovery difficult. There has been direct combustion and co-combustion of biomass. Some of the problems associated with direct combustion are high moisture content, high oxygen content, high alkaline metal content with low bulk densities (Demirbas, 2004;Khan et al., 2009). As biomass have low bulk densities, they require huge storage space and are expensive to transport these materials from one place to another. Direct combustion of dried wood or wood products and manure generate significant heating for people in Turkey (Ozcan et al., 2015).

2.5.1.2 Pyrolysis

This process is the most common thermochemical conversion among others in this category. Pyrolysis of organic residue streams such as pig manure have been extensively studied as it explores the potential to valorise these waste streams (Oyedun et al., 2013). Biochars with varying characteristics can also be generated from a diverse range of organic and agricultural materials. However the physical and chemical characteristics of biochars is greatly affected by the feedstock characteristics as well as the thermal conditions (Antal and Gronli, 2003 ; Cantrell et al., 2012 ; Novak et al., 2014). Organic components in the dried biomass is thermally decomposed at medium temperature in an inert atmosphere- absence of oxygen. Pyrolysis occurs at higher temperatures between 300-700°C (Dai et al., 2015). The process can either be slow, moderate or fast (Papari and Hawboldt, 2015). Slow pyrolysis is characterized with slow heating rates, temperature below 500°C and long solids residence times. Moderate pyrolysis involves vapour residence time between 10-20s and a temperature of about 500°C. Fast pyrolysis as the name implies has faster heating rates and less than 2s vapour residence time at a temperature of 500°C (Papari and Hawboldt, 2015). McKendry, (2002a) reported highest bio-oil (about 50-75%) with fast pyrolysis.

It is a suitable process to convert large quantities of biosolids such as animal manure and sewage sludge to energy, destroys pathogens, reduces odour as well as volume making it easy to handle, store and transport the material (Cantrell et al., 2008;Pham et al., 2013). The products of this reaction are water, biochar used for high value chemicals and biofuel, bio-oil – known as liquid fuel containing useful aromatic compounds such as xylene, toluene and benzene (Sanchez et al., 2007) and a combination of H_2 and CO_2 – known as synthesis gas to be used as fuel (Cantrell et al., 2008). The gases contain non-condensable vapour and condensable oxygenated tars which form bio-oil (Bridgwater and Peacocke, 2000).

The yields of pyrolysis products (oil, gas, char), like most other thermochemical processes, is dependent on the process conditions (temperature and residence time) as well as the feedstock used (Kuppens et al., 2014). Pyrolysis reduces waste volume significantly. During slow pyrolysis, increasing temperature, decreased the solid yield as well as the nitrogen/oxygen content of the biochar (Tsai et al., 2012). Lower temperatures and lower heating rates give a higher char yield whereas higher heating rates with intermediate temperatures result in higher oil yields (Bridgwater et al., 1999). Also, during pyrolysis, the pore properties and ash contents of the swine biochars increased as the temperature increased. In addition the biochar produced was rich in nitrogen, phosphorus, calcium, magnesium and potassium which makes it ideal as an excellent medium in the soil (Tsai et al., 2012). Bridle and Pritchard, (2004) reported 55% of nitrogen and all the phosphorus present in the raw sewage sludge was present in the char. Higher concentrations of heavy metals are present in the char although they are by far lower than the threshold for biochar quality (Monlau et al., 2016).

Pyrolysis require a pre-drying process in order to improve the thermal efficiency (calorific value) of biosolids. However, this drying stage increases the operating cost and thus is unattractive to adopt this technology in developing countries (Zhao et al., 2014a). The amount of energy is a major concern. For instance before manure is pyrolysed, it is first separated into a concentrate containing most of the potassium and nitrogen and a thick fraction which contains 18 wt% phosphorus which needs to be further dried to increase the dry matter to 70% (Kuppens et al., 2014).

Relatively dry feedstock such as beef lot manure and poultry litter are ideal for dry thermochemical processes such as incineration and pyrolysis (Cantrell et al., 2008). Pyrolysis of sewage sludge has been established mainly for energy production on a commercial scale as well (Bridle and Pritchard, 2004). As manures are nutrient-rich feedstocks, pyrolysis of these materials produces a nutrient-rich biochar unlike the plant-based biochar (Ro et al., 2010 ; Cantrell et al., 2012). Recently, biochar has been applied in agriculture to improve soil fertility (Cao and Harris, 2010). The pyrolysis char is beneficial to farmers as they could be combusted or co-combusted with other feedstocks for energy generation, earning carbon credits from carbon sequestration. The char could also be used in either existing coal or gasification plants (Cantrell et al., 2008). It is also possible to obtain active carbon either by physical activation with air or CO_2 or chemical activation with H_2SO_4, $ZnCl_2$ and H_3PO_4 (Otero et al., 2003) which could be used to eliminate odours (Inguanzo et al., 2001). It also acts as a soil amendment material which improves fertility (Antal and Gronli, 2003), animal waste chars from manure source of activated carbon (Sanchez et al., 2007). It has been shown that poultry and turkey pyrolyzed chars showed better copper ion adsorption than the commercial granular activated carbon (Lima and Marshall, 2005).

2.5.1.3 Dry gasification

Gasification of biosolids has several advantages compared to other traditional methods of waste disposal. During this process, pathogens and pollutants present in degradable waste such as sewage sludge are gasified or degraded at such high temperatures (Yu et al., 2015). Gasification eliminates treatment processes such as stabilization, digestion and composting which indicates that costs associated with these treatment processes are reduced. There are no problems associated with odour during gasification unlike when sewage sludge is applied to land. The energy efficiency during gasification is higher and causes lower gas emissions compared to incineration (Petersen and Werther, 2005;Saw et al., 2012). Furthermore, gasification produces syngas which has a wider application which could be burned in gas engines or used to produce organic chemicals and hydrogen whereas during incineration, energy is extracted only in the form of heat (Yu et al., 2015).

2.5.2 Hydrothermal processing

Hydrothermal conversion involves the application of both heat and pressure which is sufficient to keep water in the liquid state or in a supercritical state while treating the submerged biomass in the aqueous medium (Demirbas, 2001;Demirbas, 2008;Peterson et al., 2008;Zhao et al., 2013). This process was identified as an effective way of densifying the energy content in any high moisture biomass without drying it, generating useful by-products which have potential application on an industrial scale as shown in **Figure 2-4** (Zhao et al., 2014a). For instance with sludge and food wastes, the components are disintegrated, forming dissolved products which accumulate in the aqueous products (Neyens and Baeyens, 2003). During hydrothermal processing, the decomposition of solid is significantly affected by the reaction temperature rather than the reaction time as higher reaction temperatures result in higher biomass conversion to solid biofuel (Danso-Boateng et al., 2013). Hydrothermal processing simply plays three key roles: improves dewaterability, reduces the volume of biomass and energy densification. The process also destroys pathogens, removes odorous compounds, eliminates toxic metals (Reza et al., 2013).

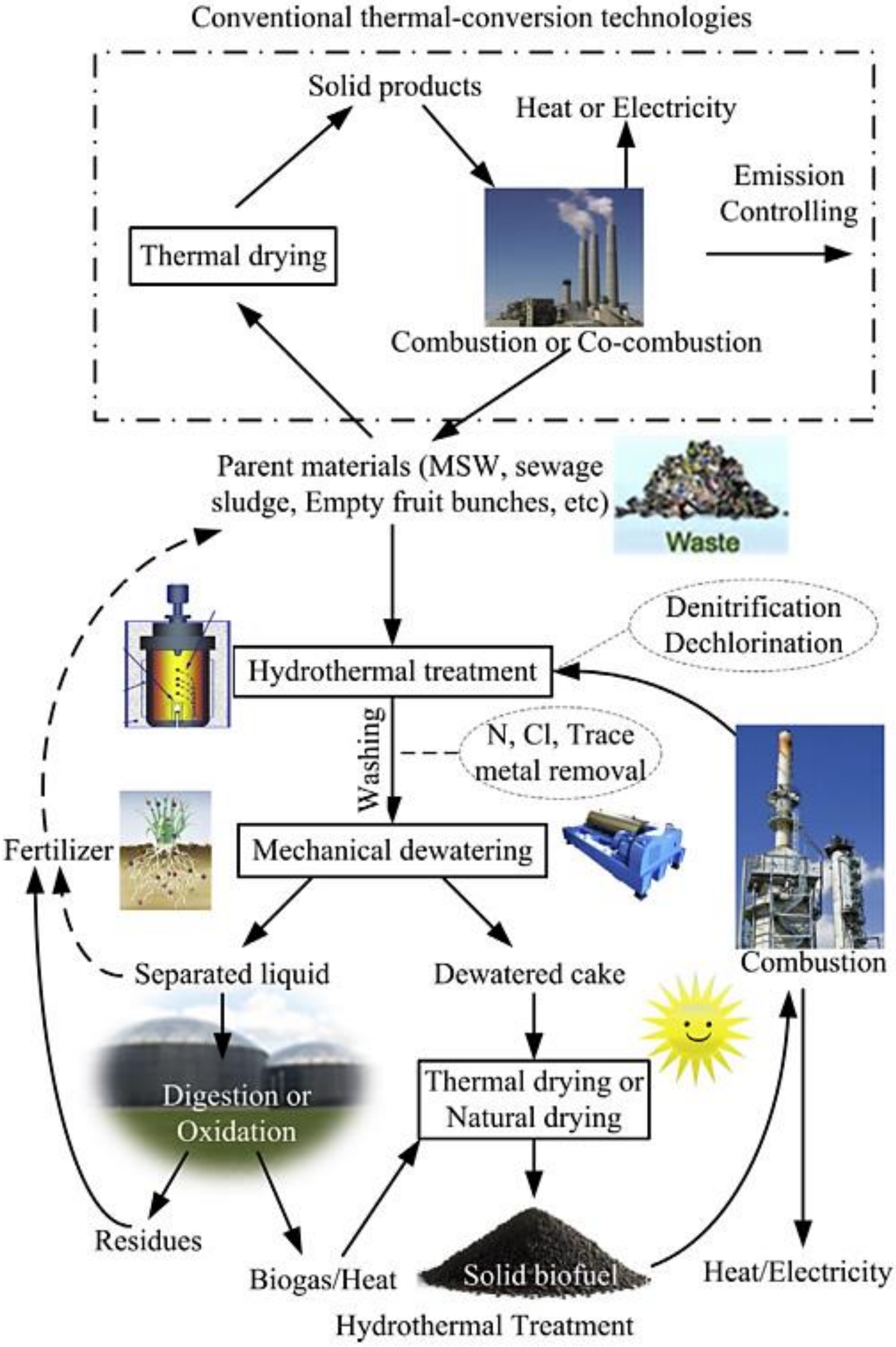


Figure 2-4: Clean solid biofuel from hydrothermal processing (Zhao et al., 2014a)

This process has received increasing interest as a pre-treatment option for biomass considering the aforementioned problems regarding their high moisture, high metal content and bulky nature. After pre-treatment of biomass, its energy density is significantly improved as well as the reduction of potassium and chlorine concentrations which are associated with severe fouling and emission of furans and dioxins respectively. Pre-treatment enables the final utilization of biomass to useful products such as biogas, animal feed, biodiesel, alcohol and bio-solid fuels (Zhao et al., 2014a).

Sufficient amount of water is a critical requirement during hydrothermal processing because the physical and chemical properties of water significantly changes with an increase in temperature; at this state, water mimics organic solvents (Watanabe et al., 2004). As the transition from sub-critical to super-critical state occurs, water changes from being a polar solvent to a non-polar solvent (Kamler and Soria, 2012). For instance at 200°C, water behaves like methanol. Ionic reactions are promoted with increasing temperature resulting in increasing saturation of both organic and inorganic components (Funke and Ziegler, 2010). The heated water also acts like a catalyst, facilitating hydrolysis, bond cleavage and ionic condensation (Funke and Ziegler, 2009). **Figure 2-5** shows the phase diagram of water. As the temperature further increases past the critical point of water, the dominating process becomes gasification (Toor et al., 2011).

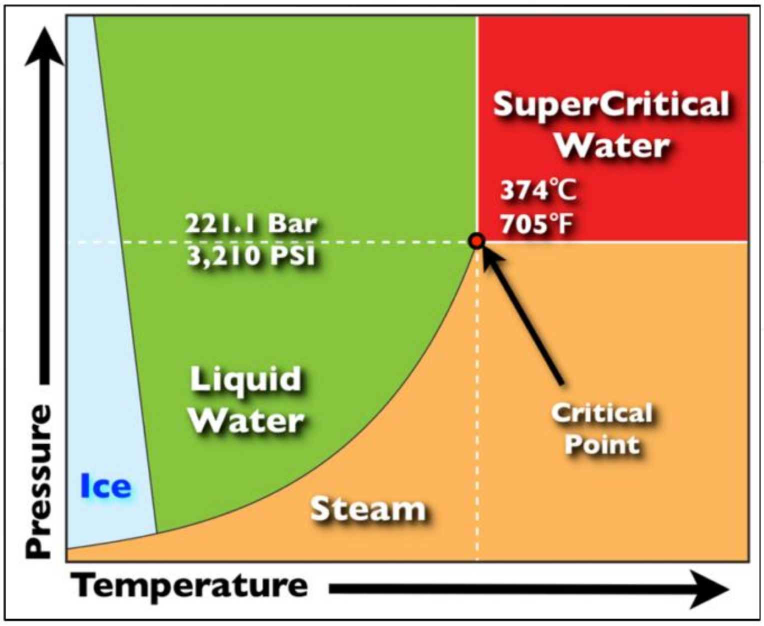


Figure 2-5: Phase diagram of water (Kamler and Soria, 2012)

2.5.2.1 Thermal Hydrolysis

Hydrolysis as a pre-treatment of sewage sludge has been proposed to improve the methane production in AD processes (Abelleira-Pereira et al., 2015). Several studies on alternative pretreatment processes for AD have been reported in (Appels et al., 2008; Wilson and Novak, 2009;Ruiz-Hernando et al., 2014). Thermal Hydrolysis (TH) using injected steam from a boiler has been highly accepted in both scientific and industrial fields and has developed to full scale in various waste water treatment plants all over the world (Morgan-Sagastume et al., 2011). The optimum conditions usually applied on an industrial scale is at 170°C for 30 minutes and a pressure of 8 bar which corresponds to the saturated steam pressure inside the reactor (Fdz-Polanco et al., 2008). It was estimated that the net electricity generated from mixed sludge using a combination of thermal hydrolysis and AD would be over 20% compared to the conventional AD process. In the study by Perez-Elvira et al., (2010), 40% higher biogas yield was achieved with mixed sludge while Donoso-Bravo et al., (2011) achieved 55% higher biogas yield using waste activated sludge. The combination of TH with AD is an energy self-sufficient process as thermal energy is needed for hydrolysis which could be obtained from the excess energy produced from the process itself Perez-Elvira and Fdz-Polanco, (2012). Thermochemical pre-treatments of the AD process have been widely explored and have been proposed as an alternative to the thermal hydrolysis process. Acid thermal hydrolysis have been studied in (Neyens et al., 2003;Liu et al., 2008, 2009) while Alkaline thermal hydrolysis have been studied in (Neyens et al., 2003;Vlyssides and Karlis, 2004;Liu et al., 2008). High pressure thermal hydrolysis of waste activated sludge (WAS) has been commercialised as it has been identified as an efficient alternative pre-treatment process for this kind of waste (Donoso-Bravo et al., 2011;Keymer et al., 2013). Thermal hydrolysis on the other hand is less severe and does not result in carbonisation or liquefaction, it is sometimes used prior to anaerobic treatment of biomass wastes (Abelleira-Pereira et al., 2015). Other low temperature hydrothermal treatments such as hot water washing have been proposed to remove inorganics from biomass thereby improving the combustion properties of biomass fuels (Saddawi et al., 2012).

2.5.2.2 Hydrothermal Carbonisation (HTC)

Hydrothermal carbonisation is a peculiar thermal conversion process which seems to be promising and an environmentally friendly waste management treatment. It is perceived to be a cost-effective method of converting biomass to useful carbonaceous materials - hydrochar, organic waste to bio-coal and organic waste to bio-oil (Titirici et al., 2012; Oliveira et al., 2013). HTC is also known for its high carbon efficiency, minimizing GHG emissions and contributing positively to carbon-foot print (Lal, 2009). During HTC, the feedstock is heated at elevated temperatures about 200°C and at a pressure higher than the saturation pressure of water (subcritical state), decomposing organic matter by a series of simultaneous reactions such as dehydration, hydrolysis, decarboxylation, aromatization and re-condensation. These series of reactions reduce the oxygen and hydrogen contents of the hydrochar produced and volatile matter is lost during the process (Lin et al., 2015). The main products obtained after HTC are solid- hydrochar otherwise known as bio-coal and an aqueous phase rich in organic compounds as well as vital nutrients which could be recycled for algal growth (Lu and Savage, 2015). These two products can be separated by simple filtration.

2.5.2.2.1 Advantages of HTC

Although HTC is not widely applied in manure treatment, it is a more competitive thermal-chemical treatment option for manure than pyrolysis because the latter is associated with drying (Dai et al., 2015). It has also been established that HTC is a better method used in handling sewage sludge with characteristic poor fuel properties capable of yielding a product with higher specific heat content making it valuable for mono incineration (Funke and Ziegler, 2010;Vom Eyser et al., 2015). The dewaterability of sewage sludge is improved with HTC. The major advantage is that HTC produces high yields of hydrochars without the need to dry the feedstock either before or during the reaction (Libra et al., 2011). Energy density in the hydrochars have been reported to be equivalent to different coal types such as lignite, brown etc (Berge et al., 2011). Also there is huge savings on energy during HTC. About 65% electric and 60% thermal energy was saved during HTC of sewage sludge on a laboratory scale (Escala et al., 2013). In addition, HTC thermally degrades and transforms emerging compounds such as endocrine disrupting compounds, pharmaceuticals, personal care products which are environmental contaminants in landfills and waste water (Berge et al., 2011).

HTC has also been identified to have beneficial application in the extraction of algal lipids from algal biomass (Heilmann et al., 2011 ; Reddy et al., 2014). One of the challenges facing the algal biofuel production is the efficient extraction of algal lipids from algal cells in an economical way (Lu and Savage, 2015). Although the two methods usually employed in lipid extraction are extraction using supercritical CO_2 and extraction using organic solvents (Halim et al., 2012). However efficient extraction using these two methods is only possible if the algal biomass is dried to obtain a low moisture algal biomass (Halim et al., 2011). Thus with HTC the cost of drying is avoided (Savage and Hestekin, 2013).

2.5.2.2.2 Application of HTC by-products

HTC significantly reduces nutrient leaching properties of hydrochar with minimal nitrogen, phosphorus and potassium leaching characteristics and therefore is a safe approach in manure management. Leaching of phosphorus from swine manure hydrochar was found to be significantly lower than swine manure pyrolyzed char and swine manure compost (Ro et al., 2016). HTC hydrochar serve as materials for catalysing CO_2 sorption, production of nanostructured materials, environmental sorbent materials, sources of energy and storage, soil amendments (Xue et al., 2012 ; Abel et al., 2013). The impact of soil-applied hydrochar on nutrient availability and retention depends on the initial hydrochar properties, the chemical and microbial interaction while the hydrochar weathers (Ro et al., 2016). Swine-manure amendments applied to land increased soil pH, carbon, nitrogen as well as extractable plant available nutrients such as P, K, Ca, Zn and Mn (Ro et al., 2016). Manure-derived hydrochar have relatively higher nutrient concentration compared to plant-based hydrochars and may be a reliable source of nutrients to crops (Ro et al., 2016).

2.5.2.2.3 Product yields and product composition after HTC

Various research on HTC have been conducted. Various feedstocks such as agricultural residues, manures, food waste, municipal solid waste, and sewage sludge could be used during the HTC process (Berge et al., 2011). The extent of carbonisation depends on feedstock composition, water to solid ratio, temperature and residence time. The solid yields and extent of carbonization is significantly changes with time (Bridgwater, 2006). In the study by Heilmann et al., (2014), the hydrochar yields from HTC of swine, poultry and cattle manure were typically about 50-60%. Hydrochar yield is strongly influenced by feedstock concentration and increases at higher feed: water ratio.

In the study by Ro et al., (2016), during HTC, volatile matter decreased from 68.5% in the swine manure feedstock to 38.0% in the hydrochar. It was significantly affected when temperature was increased from 200°C to 250°C, resulting in an increase in fixed carbon and ash contents in the hydrochar. In comparison with commercial swine manure, the hydrochar had lower volatile matter. According to Cao et al., (2013), reduction in volatile matter is usually attributed to a decrease in both proteins/peptides and carbohydrates during the conversion process. Lynam et al investigated the influence of Ca salts and acetic acid on the hydrothermal treatment of lignocellulosic biomass (Lynam et al., 2011) and identified that with acetic acid, higher calorific value hydrochar was obtainable. Reza et al have investigated the influence of acid and alkali on the hydrothermal carbonisation of wheat straw (Reza et al., 2015).

The process water from HTC is usually acidic with a pH less than 5 due to the presence of organic acids such as acetic acid produced (Lu et al., 2012). The aqueous product contains a high portion of easily oxidizable organics - total organic carbon (TOC) and chemical oxygen demand (COD) generated during carbonisation with concentrations within the levels obtained in a typical landfill leachate (Berge et al., 2011). Carbon is distributed between the aqueous product, gas phase and the hydrochar however the least amount is present in the gas phase which consists mainly of carbon dioxide from decarboxylation and traces of propene, methane and ethane while the most carbon is in the hydrochar (Funke and Ziegler, 2009;Berge et al., 2011). Increase in residence time also decreases carbon in aqueous product and increases carbon in gas phase but 45-75% carbon still remains within the solid even with an increase in time (Lu et al., 2012).

2.5.2.2.4 Distribution of inorganics and nutrients during HTC

The hydrochar contains a large fraction of the lipids which were originally present in the unprocessed biomass. Extraction of these lipids with organic solvents is very attractive for biodiesel production (Heilmann et al., 2011a). A valuable omega -3 fatty acid (eicosapentaenoic acid) could be recovered from wet algae using this approach with water and ethanol (Lu et al., 2015). It was also reported that very little amount of nitrogen was present in the extracted lipid which implies that the bulk of the nitrogen remained in the hydrochar even after extraction. Instead the lipid-extracted hydrochar is mainly composed of proteins and carbonised polysaccharides which could be used as a livestock feed supplement, raw material for carbon generation or as a soil amendment (Heilmann et al., 2011b). Extraction and recovery of nitrogen with generation of energy from the lipid extracted hydrochar is a sustainable and economical approach towards the HTC- extraction biorefinery (Lu and Savage, 2015).

HTC hydrochar also has reduced metallic species when compared to the raw unprocessed biomass as most of the nutrients and leached inorganics are present in the aqueous product (Du et al., 2012;Liu et al., 2013). In the study by Levine et al., (2013), the aqueous product recovered from HTC of algal biomass – *N. oculata* supported algal growth thereby reducing the capital costs associated with algae cultivation. Manure-derived hydrochar has been reported to have reduced nitrogen content compared to the raw swine manure (Ro et al., 2016). Although nitrogen content is reduced in the algae-derived hydrochar, the form of nitrogen is similar to the form of nitrogen in the starting algae feedstock (Heilmann et al., 2010 ; Levine et al., 2013). Previously, during HTC of microalgae and distillers grain, most of the phosphorus in the feedstock was mostly present in the aqueous product as soluble phosphate (Heilmann et al., 2011a, 2011b). However it was the opposite with manures as during HTC the majority of phosphorus was in the solid product (Heilmann et al., 2014). They attributed this to the presence of multivalent cations such as Mg, Ca, Al, Fe were responsible for the formation of insoluble phosphates in colloidal form or electrostatically bound to proteins in manures. The total concentrations of metal ions were 2.60%, 3.16%, 5.09% for cattle, swine and poultry manure whereas it was less than 0.5% in microalgae and distillers grain and therefore insufficient to form significant insoluble phosphates in the hydrochar (Heilmann et al., 2011a, 2011b). Also the formation of insoluble phosphate increased the ash content by 85%, 60%, 69% for cattle, swine and poultry manure derived hydrochar (Heilmann et al., 2014).

2.5.2.3 Hydrothermal Liquefaction (HTL)

Hydrothermal liquefaction is a innovative technology for converting wet waste biomass or aquatic biomass into liquid biofuel and valuable chemicals (Cantrell et al., 2007). The process occurs at temperatures between 250°C-350°C and pressure between 5-20 MPa high enough to keep water in its liquid state. At this subcritical state, water is capable of catalyzing both acidic and basic reactions by dissociating into hydrogen ion (H^+) and hydroxyl ion (OH^-) (Harvey and Friend, 2004). Macromolecules present in the biomass are broken down into dark viscous biocrude with high heating value, solid residue or char, gaseous fraction and aqueous product containing nutrients, inorganic species and polar organic compounds (Shakya et al., 2015). At subcritical condition, the equilibrum constant of water between 200°C-300°C increases to 10^{-11} compared to 10^{-14} at room temperature (Marshall and Franck, 1981). Also the polarity of water decreases, thereby promoting organic reactions which would normally occur in non-polar solvents (Harvey and Friend, 2004).

The yields of biocrude against the conversion temperature vary with different biomass feedstocks. The pathway for biocrude formation is shown in **Figure 2-6** where biomass containing lignin, cellulose and hemicellulose is initially hydrolysed to simple sugars such as glucose and fructose at minimum of 250°C. At 250°C, 60% lignin, 100% hemicellulose and 22% cellulose are converted to simple sugars. At higher temperatures above 250°C, hemicellulose and cellulose are converted to biocrude while lignin degrades faster at 300°C but re-polymerises occur almost at the same time. Therefore temperature of 300°C or above is ideal for maximum biocrude yield (Yin et al., 2010). At even higher temperatures, the biocrude formed decomposes to gas and tar.

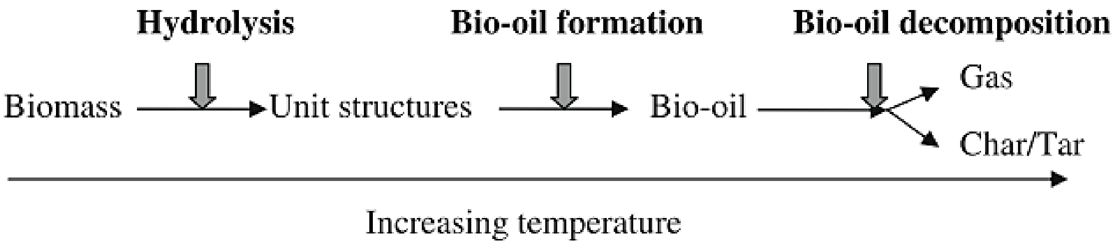


Figure 2-6: Simple pathway for hydrothermal liquefaction of biomass (Yin et al., 2010)

There are several approaches of obtaining liquid fuel from algae in a HTL algal biorefinery. The biomass is either converted directly to biofuel or to valuable compounds first before converting the biomass to biofuel. Lopez Barreiro et al., (2014), suggested that extracting proteins first before converting the residue to biofuel is a more economical and reduces the nitrogen content in the biocrude which is a major problem. Draaisma et al., (2013) explored the market opportunities of extracting high value compounds from algal biomass for feed, food and chemicals prior to HTL.

2.5.2.3.1 Influence of process conditions on HTL yields

Various feedstocks such as wood chippings (Boocock and Poretta, 1986), sewage sludge (Yokoyama et al., 1987;Itoh et al., 1994), microalgae (Dote et al., 1994; Brown et al., 2010; Biller and Ross, 2011), swine manure (He et al., 2000), cattle manure (Yin et al., 2010), residual lignin material (Demirbas, 1991), garbage (Minowa et al., 1995) and woody biomass (Xu and Lad, 2007) have been used as feedstock for the HTL process. Like the HTC, HTL does not require the feedstock to be pre-dried as water acts as the reaction medium.

Research studies on process variables such as temperature, residence time, heating rate using different algae strains have been performed primarily to improve biocrude yields (Brown et al., 2010;Anastasakis and Ross, 2011;Jena et al., 2011;Garcia Alba et al., 2012). In most of these studies, biocrude yield increased with temperature up to 350°C beyond which it reduces. Some others studies have reported maximum yield at 320°C (Valdez et al., 2012) and 375°C (Garcia Alba et al., 2012). These variations in temperature are attributed to differences in the feedstock biochemical composition (lipids, proteins and carbohydrate content). Biller and Ross, (2011) studied the influence of biochemical content on biocrude yield. Ocfemia et al., (2006) investigated the effect of operating parameters on biocrude yield and quality using a continuous mode. Even though HTL is a promising route with waste disposal benefits, there is still a major setback with optimization and other downstream processes as varing biocrude chemistry could occur during the process (Vardon et al., 2011).

Several studies have shown that bio-oil yield and quality increase with the addition of alkaline catalyst and also suppresses the formation of char. The study by Ogi et al., (1985) was on HTL of wood using various alkaline catalysts namely $Ca(OH)_2$, $CaCO_3$, NaOH, K_2CO_3, KOH, Na_2CO_3 between 300 - 350°C. They observed that 50 wt.% bio-oil was produced with NaOH while 22.2 wt.% was obtained with no addition of catalyst. In a study by Karagoz et al., a similar effect with catalyst was observed with pinewood (Karagoz et al., 2006). In the study by Shakya et al., (2015), HTL using Na_2CO_3 at 300°C and 350°C increased the biocrude obtained from algae strains- *Pavlova* and *Isochrysis* with high carbohydrate content whereas higher biocrude from high protein algae-*Nannochloropsis* was obtained at 250°C. Maximum biocrude (47 wt %) was obtained from *Pavlova* at 350°C.

Vardon et al., (2011) conducted HTL on different feedstocks such as swine manure, *Spirulina* algae and digested sludge at 300°C and pressure between 10-12 MPa for 30 minutes. They investigated the influence of feedstock composition on the properties and physico-chemical properties of the biocrude produced. The highest yield (32.6%) was obtained from *Spirulina* while the lowest yield (9.4%) was obtained from digested sludge. The biocrude products from these three feedstocks had similar higher heating value between 32.0 and 34.7 MJ/kg but different biocrude chemistry.

Yin et al., (2010), studied HTL of cattle manure with NaOH. They observed maximum bio-oil yield of about 48.78 wt.% at 310°C with CO process gas, 15 minutes residence time and 0.25 feed to water ratio. They concluded that the bio-oil yield was dependent on the temperature and process gas used. Longer residence time, higher feed to water ratio, higher initial conversion pressure decreased bio-yield as these conditions converted bio-oil to gases and tar/char.

2.5.2.3.2 Product composition after HTL

The biocrude contains a wide range of chemical compounds such as carboxylic acids and its derivatives - α and β unsaturated ketones aromatics, phenol derivatives, poly alcohols, esters, nitrogenous ring compounds, straight and branched aliphatic compounds but not C_{4-15} alkane which are the major constituents in diesel and gasoline (Yin et al., 2010 ; Biller and Ross, 2011).

As a result of the diverse compounds present in the biocrude, it is does not have storage stability, has low response to upgrading processes while the combustion performance and economic value are also affected (Huber et al., 2006). The proportion of protein, carbohydrate and lipid in the unprocessed feedstock influences the distribution of chemical compounds and functional group chemistry in the biocrude (Biller and Ross, 2011 ; Vardon et al., 2011). HTL biocrude differs from petroleum crude oils as it contains about 10-20% oxygen, 4-6% nitrogen and sulphur which results in unwanted qualities such as high viscosity, acidity and polymerization (Adjaye et al., 1992; Peterson et al., 2008;Shakya et al., 2015). The presence of nitrogen and sulphur is a disadvantage and needs to be upgradedfor use as a petroleum oil to avoid emission of greenhouse gases on combustion (Elliott, 2007; Cantrell et al., 2008; Duan and Savage, 2011). Although the emissions from unprocessed biocrude contributes less greenhouse gases to the environment unlike the fossil fuels (Yin et al., 2010).

Nitrogen is present in the biocrude as a result of protein degradation in the biomass feedstock (Torri et al., 2012). However other forms of nitrogen exist in the biocrude apart from those generated during protein hydrolysis and may have originated from nitrogen – containing molecules in the biomass (Lopez Barreiro et al., 2014). In the study by Klingler et al., at 300°C and 350°C, it was observed that protein degradation increased with increasing temperature (Klingler et al., 2007). As reported by Lopez Barreiro et al., increasing the temperature from 300°C and 375°C reduced the nitrogen content in the biocrude (Lopez Barreiro et al., 2014). They observed that 30 - 40% of the nitrogen present in *N. gaditana* and *S. almeriensis* feedstock was present in the biocrude but nitrogen was not detected in the gas product. Protein extraction from biomass prior to HTL reduces the nitrogen in the biocrude and increases biocrude yield while lipid extraction of the algal biomass reduces the quality of biocrude as it increases the fraction of protein present thus increasing nitrogen content (Lopez Barreiro et al., 2014).

There are several reports on hydrothermal processing of microalgae- *Botryococcus braunii*, *Microcystis viridis*, Spirulina, and *Dunaliella tertiolecta*. Most liquefaction studies were performed between 200-350°C at 5-60 minute residence time. Biocrude yields were between 35-65 wt% with typical high nitrogen –about 6% and high oxygen –about 12 wt%. The heating value is usually between 35-50MJ kg^{-1}. HTL of *Microcystis viridis* produced gas which was mostly CO_2 and CH_4 and small amounts of CO and H_2 (Brown et al., 2010).

2.5.2.3.3 Distribution of inorganics and nutrients during HTL

The aqueous product from HTL is semi-transparent and alkaline with a characteristic foul smell due to the presence of ammonia – a weak base (Shakya et al., 2015). For catalytic HTL, the aqueous product pH is between 8-9.5 which is likely due to the presence of alkali catalyst while it is between 7-8 for non- catalytic HTL (Ross et al., 2010;Shakya et al., 2015). It contains a significant proportion of organics which is indicated by the presence of TOC (Anastasakis and Ross, 2011) and also contains glycerol, acetate and formate which are by-products of carbohydrate hydrolysis (Ross et al., 2010). Organic carbon decreases with increase in temperature as most of the carbon is converted into biocrude and gas (Shakya et al., 2015). Catalytic HTL of *Nannochloropsis* and *Pavlova* with Na_2CO_3 resulted in higher TOC levels at 300°C and 350°C shifting non-volatile organic carbon into the aqueous product with reduced residue formation (Shakya et al., 2015). A similar observation was in the study by Yang et al., (2004).

During HTL, recovery of nitrogen is greatly associated with the aqueous product (about 50%) than any other products (Lopez Barreiro et al., 2014). Other studies have ascertained that during HTL of microalgae, a large proportion of the nitrogen and phosphorus initially present in the feedstock are found in the aqueous product (Yu et al., 2011;Yu et al., 2014). The levels of total nitrogen extracted into the aqueous product depends on the processing temperature, type of strain/feedstock used and the biochemical content of the strain/feedstock. In algae, nitrogen is present in the form of protein and decomposes into ammonia and soluble amino acids during HTL (Biller and Ross, 2011). During low HTL processing of *Desmodesmus sp.* microalgae, about 40% of aqueous nitrogen was in the form of NH_4^+ while nitrogen –containing organic compounds such as heterocycles were present in the remaining portion (Garcia Alba et al., 2013). However an increase in HTL temperature, would degrade these organic molecules, increasing the nitrogen levels with the formation of more NH_4^+ in the aqueous product with an increased partition of carbon in both the biocrude and the gas phase. However this is mainly influenced by the type of strain used. For instance during HTL of *N. gaditana* at 375°C, 90% of the nitrogen was present as NH_4^+ in the aqueous product (Lopez Barreiro et al., 2014).

Increased deamination reaction occurs when temperature is increased, converting nitrogen compounds in the bio-oil to ammonia which is soluble in the aqueous product. A similar observation was in the study by Yang et al., (2004) however this was not the case with catalytic runs. In the study by Ross et al., (2010), for *Spirulina*, nitrogen concentration decreased with temperature while with *Chlorella*, no increase or decrease was observed. Muangrat et al., investigated the presence of ammonia in the gas phase after HTL of whey- a dairy industry waste performed at 300°C, 330°C and 350°C. At 0min, the amount of NH_4^+ was zero, 0.13mg and 1.00mg respectively while 4.60mg of NH_4^+ was obtained at 330°C for 60 minutes. It was concluded that increasing residence time increases the amount of ammonia in the gas phase although these concentrations were insignificant compared to the dissolved ammonia in the aqueous product (Muangrat et al., 2011).

The fate of P during HTL is closely linked to the metal composition of the feedstock as feedstock high in calcium or magnesium will favour precipitation of the P in the solid product (Yu et al., 2014). This is in agreement with the immobilisation of P as described by Heilmann et al., (2014). In the study by He et al., nitrogen, phosphorus and potassium (NPK) were mainly present in the aqueous product and changing the reaction conditions as well as increasing temperature from 275°C to 350°C did not affect the distribution of these nutrients (He et al., 2000).

The recovery of inorganic matter depends on the type and concentration of other inorganic materials in the feedstock as tend to affect the reaction conditions influencing the point at which the salts would precipitate as solid (Lopez Barreiro et al., 2014). Recovery of divalent ions such as Mg^{2+} and Ca^{2+} in the aqueous product following HTL was below detection limit and would have most likely been precipitated in the solid product while monovalent ions such as K^+ and Na^+ were almost completely recovered in the aqueous product and could be recycled (Lopez Barreiro et al., 2014). However they found that there was variability with the recovery of sulphur as sulphate was strain dependent.

2.5.2.4 Supercritical Water Gasification (SCWG)

Supercritical water gasification has been studied as a promising process for hydrogen generation (Momirlan and Veziroglu, 2005;Kruse, 2009) even though other techniques have been reported (L. Wang et al., 2008).

As shown in **Figure 2-5**, supercritical water gasification occurs above 374.15°C and pressure above 22.1 MPa in which organic matter present in the original feedstock undergoes hydrolysis, pyrolysis and other series of reactions, generating hydrogen gas (Zhu et al., 2011). Water at supercritical state acts as a both a solvent for organic compounds and as a reactant to generate hydrogen gas. SCWG has also received increased attention as a potential technology for bio-based waste such as sewage sludge offering a cost - effective disposal alternative and optimum resource utilization (Matsumura et al., 2005 ; Muangrat et al., 2010).

Most studies on SCWG have focused on energy recovery (Zhang et al., 2010 ; Yun et al., 2012) and the use of catalyst to promote hydrogen yield with sludge (Guo et al., 2010 ; Acelas et al., 2014), wood (Yamaguchi et al., 2009). Hydrogen production has been enhanced using various catalysts and additives such as noble metals (e.g. platinum, ruthenium or nickel), activated carbon, metal oxides and alkali catalysts (e.g. $Ca(OH)_2$, $KHCO_3$, K_2CO_3, KOH, NaOH and Na_2CO_3). Catalysts have been used even to enhance gas production at low temperature of about 450°C (Muangrat et al., 2011, 2010b). These additives have become attractive as they give higher hydrogen yields and inhibit the formation of tar or char (Xu et al., 2013). In the past decade, other research studies were focussed on temperature, pressure, residence time (Xu et al., 2013), catalyst poisoning (Elliott et al., 1993), salt precipitation (Xu and Antal, 1998 ; Schubert et al., 2010). Salt precipitation is one of the major setbacks with commercializing SCWG technology as it causes plugging or fouling of the system (Hodes et al., 2004). Zhu et al., studied the behaviour of phosphorus and the forms of phosphorus in the products obtained after gasifying sewage sludge at sub and supercritical conditions

(Zhu et al., 2011). In addition they investigated the effect of dry matter content, residence time, reaction temperature, reaction pressure on the form of phosphorus and conversion of phosphorus.

In comparison with the conventional gasification technology, SCWG can accommodate wet biomass having up to 75-95% moisture without pre-drying (Xu et al., 2012). SCWG has a higher gasification efficiency as supercritical water tends to suppress the formation of char and tar (Matsumura et al., 2005). An overall conversion efficiency of 97.8%, 99.9% and 98.2% at 400°C, 450°C and 500°C respectively have been reported (Zhu et al., 2011). Chakinala et al., performed SCWG of *Chlorella vulgaris* and observed that the gas composition was made up of CH_4, H_2, CO, CO_2 and C_2-C_3 compounds. They concluded that higher gasification efficiencies were achieved with low algae concentration, at high temperatures and longer residence times (Chakinala et al., 2010). In the study by Muangrat et al., increasing feed (whey) concentration significantly reduced H_2 production while it increased the amount of CO_2, CH_4, CO and other hydrocarbon gases (Muangrat et al., 2011). The highest H_2 was produced with 5% w/v feedstock and no CO_2 or CO was detected. Previous studies have shown that increasing SCWG temperature increased the degree of reaction and produced a lot more hydrogen however the higher energy input required remains the downside of the process (Xu et al., 2013). Although even more energy is required in conventional 'dry' gasification (Kruse, 2008).

2.5.2.4.1 Application of SCWG by-products

As stated by Nakamura et al., organic components in feedstocks such as poultry manure are completely gasified into hydrogen (H_2), methane (CH_4), carbondioxide (CO_2) and ethylene (C_2H_4) (Nakamura et al., 2008). Amongst other gases produced during SCWG, H_2 could be separated and used in the hydrogenation of unsaturated lipids for biodiesel refinery (Lu and Savage, 2015). Hydrogen gas can be used in fuel cells as well.

2.5.2.4.2 Distribution of inorganics and nutrients during SCWG

A number of reports have shown that aqueous products from high temperature hydrothermal processing such as HTL and SCWG contain significant amounts of nutrients (Tsukahara et al., 2001;Jena et al., 2011;Biller et al., 2012;Cherad et al., 2013;López Barreiro et al., 2015) which could be recycled to cultivate fresh microalgae with high lipid content and beneficial for biofuel production (Biller et al., 2011). Lu and Savage performed SCWG of lipid extracted hydrochar from *Nannochloropsis sp* at 450 - 600°C to recover energy as fuel gases. They observed that organic bound nitrogen present in the hydrochar was converted to ammonium in the aqueous product and concluded that ammonium was formed during hydrolysis and elimination reactions which involved water molecules (Lu and Savage, 2015). After SCWG at 600°C and 6 hours, about 94% total nitrogen was present in the aqueous product which was mainly in the form of NH_3-N (97%). Even at lower SCWG temperatures of 450 - 550°C, almost a 100% total nitrogen was recovered. Generally, NH_3-N and energy recovery increased with temperature severity. At 450°C and 10 minutes residence time, 64% NH_3-N recovery was obtained in the aqueous product while at 550°C and 90 minutes retention time, NH_3-N recovery was 90%. They concluded that at more severe conditions convert the N-containing compounds present in the aqueous product to ammonium. They concluded that the characteristic light yellow colour of the aqueous product from SCWG 450 - 550°C was due to the presence of amino acids produced during SCWG process while complete gasification of these N-containing molecules to ammonium was responsible for the colourless aqueous product from SCWG at 600°C (Lu and Savage, 2015). Phosphorus is not in the gas phase after SCWG (Yildiz Bircan et al., 2011).

Lopez Barreiro et al., observed that higher ammonium was present in the aqueous product following gasification when compared to the levels in the aqueous product from liquefaction. Also the levels of extracted phosphate in the process water were found to vary with feedstock and once again are linked to the inorganic content of the feedstock (Lopez Barreiro et al., 2014). The aqueous product also contains phenols and the addition of K_2CO_3 in increasing concentrations from 0 to 8 wt% has been shown to decrease phenol concentration from 14.9 to 11.0 mg/L (Xu et al., 2013).

In the study by Zhu et al., the concentration of TP in the aqueous product decreased with increasing temperature from 400 to 500°C; other forms of phosphorus decreased from 2.85 to 0.57 mg P/L (Zhu et al., 2011). Although dissoluble reactive phosphorus (DRP) was observed to have increased which implies that organic -P was almost completely converted to inorganic-P at 500°C. However the form in which inorganic-P exist in the aqueous product is dependent on the aqueous pH (Zhu et al., 2011). An increase in pressure from 20.5 to 23.5MPa also increased the concentration of TP from 43.8 to 67.1 mg P/L, DRP from 42.6 to 64.3 mg P/L and other forms of phosphorus.

The recovered solid residue from the SCWG process has high coke concentration of about 10wt% which is most likely due to carbonisation reaction occurring during the process (Xu et al., 2013). Zhu et al., reported that phosphorus was almost completely associated with the solid residue, increasing TP from 90.1% to 96.6% for all the SCWG conditions performed. The apatite-P fraction of the solid increased from 2.9% to 45%. Apatite-P in the raw sludge increased from 0.404 mg-P/g to 10.6 mg-P/g in the solid residues. As organic-P is being degraded with dissolution of non-apatite –P in the aqueous product, apatite-P increase in the solid product. They also observed that at 60 minutes residence time and 9.1% dry matter content, TP in the solid product increased with increasing temperature. Increasing residence time from 5 to 60 minutes also significantly increased TP in solid from 14.1 mg-P/g to about 20.6 mg-P/g (Zhu et al., 2011). At 5 minutes residence time, organic-P was significantly reduced with no significant change in concentration at longer residence times. Increase in pressure from 20.5 to 23.5MPa at 400°C also significantly increased the apatite-P from 9.98 to 11.1 mg-P/g and also the non-apatite-P from 9.45 to 10.3mg-P/g. Finally, it was observed that higher organic matter (16.7 wt%) did not favour the conversion of organic phosphorus but increased the non-apatite-P in the solid residue. Higher conversions were achieved with 4.8-9.1 wt% dry organic matter.

As stated by Yanagida et al., in addition to phosphorus, other inorganic species such as calcium and silicon move into the solid product after SCWG treatment whereas all potassium, nitrogen and chlorine move into the aqueous product. Therefore recovery of calcium and phosphorus from the solid product is necessary (Yanagida et al., 2009). Also as nitrogen is the predominant element present in the aqueous product, it is an indicator of wastewater quality therefore it should be recovered or converted to other useful compounds (Yanagida et al., 2009).

2.6 Recovery of nutrients from thermochemical conversion processes

As the global population is increasing at a phenomenal rate, one of the most formidable problems is the availability of phosphorus with increasing demand and its sustainability (Cordell et al., 2009a). Phosphorus is one of the most vital elements essential to life as it is an integral part of most biological building blocks. It plays a key role in cell metabolism of every living organism and has no substitute in biochemical processes which makes humans rely on its availability. Phosphorus is mostly mined from phosphate rocks which are non-renewable sources (Bridle and Pritchard, 2004). Besides, there are limited high-quality phosphate rocks which are increasingly being explored on a global scale. Phosphate rocks are a mixture of apatites and calcium phosphate which is insoluble in water and cannot be directly used as fertiliser unless treated with acid to form soluble superphosphates – an effective fertiliser compound (Wilson, 1969). As a result of its limited availability, there are implications on global food security as it is relevant to secure food availability for the increasing growing world population which is expected to reach 9 billion by 2050 (Cordell and White, 2011).

The key features of phosphorus are as follows (Cordell and White, 2011):

- It is the 11th most abundant element yet it is essential to all forms of life-plants, animals, bacteria and a vital component of DNA, RNA and ATP which is an energy carrier to the brain.
- It is essential in food production as it is a limiting nutrient for plant growth and no element can substitute its relevance. Hence it could limit global crop yields.
- It can neither be manufactured nor destroyed.
- Phosphorus reserves are only in some geographical regions. For instance Japan has no natural phosphorus reserve and imports the phosphate rocks used (Kaikake et al., 2009).
- Phosphorus is not significantly present in gaseous phase and cannot be circulated unlike carbon, hydrogen, nitrogen and oxygen.
- Global demand for phosphorus is increasing.

2.6.1 Forms of phosphorus during hydrothermal processing

Phosphorus extraction and retention from any feedstock depends on its existing chemical form which could either be as a mineral, pyrophosphate or orthophosphate and also its combination with metal ions (Mcdowell and Condron, 2000;McDowell et al., 2002). They found that mobile forms of phosphorus are either soluble P species or the weakly adsorbed ones on Ca, Fe and Al. The transformation and combination of P as Ca-P, Fe-P and Al-P causes a decrease in the water-extractable phosphorus (Sharpley et al., 2004). As stated by (Qian and Jiang, 2014), four forms of P namely orthophosphate, pyrophosphate, orthophosphate monoesters and orthophosphate diesters are present in sludge, however the organic fraction mainly consists of orthophosphate monoesters and diesters (Cade-Menun, 2005).

2.6.2 The phosphorus cycle

Figure 2-7 shows the phosphorus cycle in nature and the various routes by which phosphorus enters the water bodies. One route is from the weathering of the phosphate rocks which results in the deposition of dissolved phosphates in the marine sediments or in the marine algae which could be eaten by some aquatic animals. During mining activities, phosphates are mined and used for the manufacture of fertilisers. Phosphates present in these fertilisers are deposited in farmlands and sometimes washed into the water body during rainfalls or crops eaten up by grazing animals. When these animals die or excrete, their carcasses and manure are deposited on the land as well.

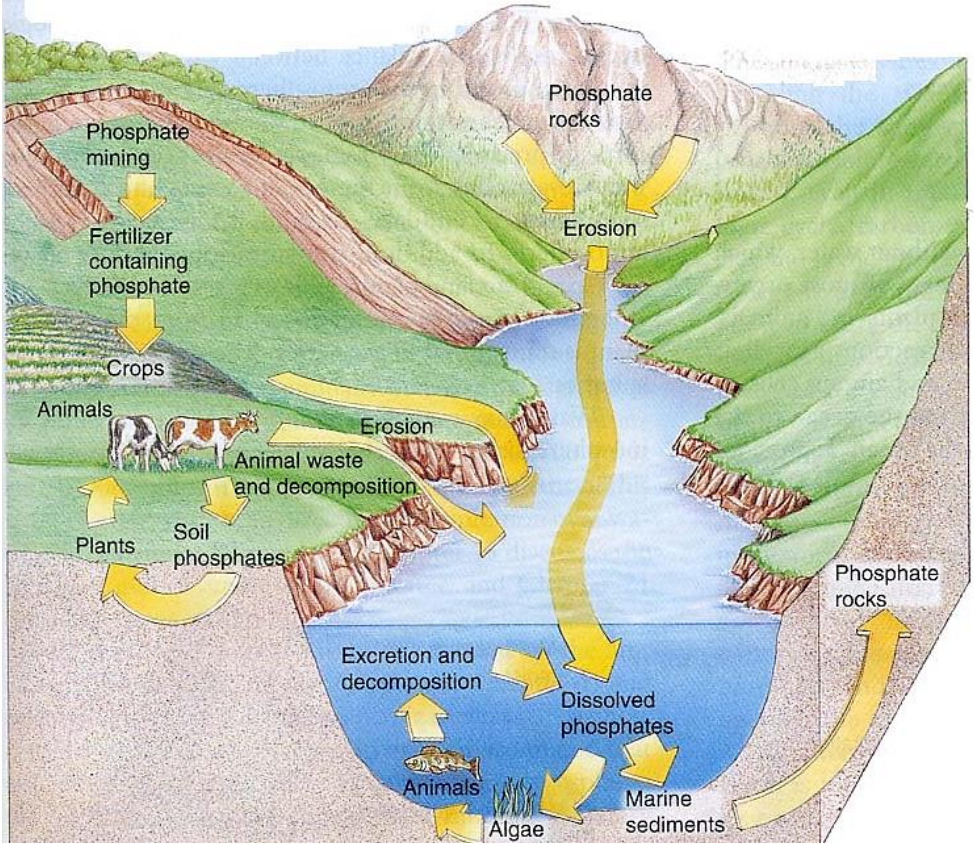


Figure 2-7: The phosphorus cycle in nature (EOI, 2011)

2.6.3 Phosphorus recovery methods

Even though huge quantities of phosphorus is produced each year, optimization of phosphorus in food production and consumption is lacking as only a fifth of the total quantity produced is consumed as food in the world (Cordell et al., 2009a). Phosphorus is lost either temporarily or permanently at every stage of food production which is not beneficial for the long term goal to recover as much phosphorus in future in order to secure food production. As a result of this, various management strategies such as integrated phosphorus recovery and reuse coupled with strategic policies, partnerships and investment in physical structure should be put in place, backed by policies in order to avoid such losses (Cordell and White, 2011). There has been increased research into various methods to close the phosphorus loop (Cordell et al., 2009a). For countries like Japan, shortage of phosphorus will pose a serious problem. Therefore there is need to develop methods/technologies to reclaim phosphorus. Consequently, this has stimulated new technologies and has provided economic opportunities for phosphorus recovery from wet waste, especially technologies that produce nutrient-rich by-products which could compete favourably with mineral fertilisers.

More so, re-use of recovered phosphorus would also reduce phosphorus losses to the environment and provides sustainability of animal production for food. Recoverable phosphorus is referred to as the quantity of nutrient available after nutrient losses during collection, storage and treatment which can either be applied on land or utilized by any other means (Kellogg et al., 2000). Recoverable phosphorus from poultry manure contributes about 39% of the total recoverable phosphorus from animal manures in the U.S (Gollehon et al., 2001).

Regardless of whether phosphorus shortage impacts the world sooner or later, it is important to develop reclamation processes. Phosphorus recovered in a concentrated usable form is essential to agriculture as it is a major ingredient in many artificial fertilisers (Azuara et al., 2013; Szogi et al., 2015). Many phosphorus recovery methods from solution have been reported. One is mixing calcium salt solution with phosphate solution to synthesize hydroxyapatite $Ca_5(PO_4)_3(OH)$ (Weng and Baptista, 1998;Pang and Bao, 2003). Recently, there has been growing interest towards the recovery of phosphorus as struvite- magnesium ammonium phosphate ($NH_4MgPO_4.6H_2O$) from waste and wastewater (Li et al., 1999;Nelson et al., 2003;Suzuki et al., 2005). Anaerobic treatment of pig manure and recovery of phosphorus via struvite precipitation from the digestate has been investigated (Karakashev et al., 2008). Also recovery of phosphorus as phosphoric acid using solvent extraction has been reported (Kaikake et al., 2009). Phosphorus in sewage sludge ash was extracted with HCl, then ammonium solution was added to precipitate aluminium phosphate which is dissolved with HCl to extract phosphoric acid. Afterwards, phosphoric acid was extracted with tri-n-butyl phosphate.

There has been a number of physical, chemical and biological processes which have been identified as potential routes to recover phosphorus from animal manure and biosolids in general (Szogi and Vanotti, 2009). Methods such as immobilization of phosphorus in manure by the addition of aluminium and calcium have been developed to precipitate phosphorus (Wagner et al., 2008). In the case of wastewater treatment processes, recovery of phosphorus in the sludge is one of the key stages of the treatment plant in order to reduce the nutrient load being discharged into the water body, if not eutrophication would be inevitable (Driver et al., 1999). Although phosphorus recovery from wastewater seems to be the most common with increasing attention, other organic wastes such as human urine, faeces, food waste, agricultural/ crop residues, animal manure, carcasses, detergents and other industrial wastes could contain this element as well. Phosphorus recovery techniques from waste streams can either be grouped into recovery from liquid phase and recovery from solids such as incineration ash and sludge ash (Desmidt et al., 2015). The most common method of recovering phosphorus from liquid phase manure is by using crystallizers and fluid bed reactors seeded to improve aggregation of phosphate particles and efficient separation by filtration (Karunanithi et al., 2015).

2.6.3.1 Recovery of phosphorus from solids by precipitation

- **Recovery from incineration ash**

Incineration of waste has been applied on commercial operation especially in regions where land disposal is prohibited. However, the generation of huge amounts of ash and the associated high cost of ash disposal has prevented economics of wide spread incineration. As a result, the use of incineration ash has been explored as a resource. Phosphorus can be recovered from incineration ash in two ways; the wet process using acid or organic solvents for extraction with subsequent precipitation or the dry process by melting the ash. However this is more energy intensive.

In the study by Kaikake et al., (2009), phosphorus was recovered from chicken manure incineration ash (about 8% phosphorus) using a two-step process- acid dissolution and alkali precipitation. First the ash was treated with acid-1M HCl to obtain phosphorus-rich solution, and phosphorus was recovered by precipitation by changing the pH to 3, 4 and 8 using NaOH. A small amount of phosphorus was precipitated at pH 3 to remove iron and filtered afterwards. At pH 4, 84% of phosphorus was recovered as $CaHPO_4.2H_2O$ having 92% purity. The remaining phosphorus was recovered as hydroxyapatite at pH 8.

- **Recovery from biochar**

Hydrothermal processing has been shown to reduce the solubility of phosphorus in the treated waste biomass suggesting that these emerging technologies are promising routes to reduce phosphorus loss to the environment from land application of manure (Liang et al., 2014). There has been much interest in recovering phosphorus from solid animal manure by wet extraction of phosphorus present in the byproducts of thermal treatment. Several studies have focussed on phosphorus release properties of biochar (Angst and Sohi, 2013; Wei et al., 2013; Liang et al., 2014) while Dai et al., (2015) studied the speciation and solubility of phosphorus from biochar obtained from HTC of cow manure. In the study by Azuara et al., (2013), phosphorus was recovered from biochar derived from the pyrolysis of pig manure. The biochar contained about 92-97% of the phosphorus present in the fresh manure. About 60 - 75% inorganic phosphate – ortho phosphate and 90% total phosphorus was extracted using 0.2M sulfuric acid solution. Acidifying ash or char is more economical than acidifying the fresh manure as less acid is used to solubilize phosphorus.

Pyrolysis has been developed for the treatment of sewage sludge (Viana et al., 2015). As sludge nutrients concentrate in the pyrolysis char, Bridle and Pritchard, (2004) investigated the nutrient value of pyrolyzed sewage to plant growth by performing soil incubation experiment for 56 days. It was observed that the phosphorus in the char was bioavailable, but releases slowly while the nitrogen was insoluble. The char had lower percentage of water-soluble P compared to the dried sludge pellets or sludge derived digestate. Huang and Tang, (2015) also confirmed that not all the phosphorus in the char is bioavailable.

As HTC immobilises most of the phosphorus in the hydrochar, it has been identified as a route to reclaim phosphate for use in agriculture (Heilmann et al., 2014;Dai et al., 2015). Generally speaking, immobilisation of phosphorus in the hydrochar is feedstock dependent and largely associated with the inorganic content of the feedstock (Ekpo et al., 2016; Dai et al., 2015). Heilmann et al, indicated that up to 90% of the total phosphorus initially present in swine, cattle and poultry manure feedstocks is concentrated in the hydrochar as precipitated phosphate salts. In order to recover this, they proposed acid extraction of the hydrochar followed by subsequent precipitation of phosphorus with alkali (Heilmann et al., 2014). They achieved 81-87% phosphate recovery after acid treatment of the hydrochar and addition of a base to a pH of 9. The precipitate formed was calcium phosphate.

SCWG is a potential route for phosphorus recovery as the solid product contains most of the phosphorus in the feedstock. In the study by Yanagida et al., the recovery of elements such as calcium, phosphorus and nitrogen in solid and aqueous products obtained from SCWG of poultry manure was investigated. Activated carbon was used as catalyst for the process. It was observed that the solid product was mainly composed of carbon (57%) however with treatment using 1N HCl, the carbon content increased to 73%. Only 12 wt% phosphate content was present in the solid product recovered directly from SCWG. After acid treatment of the solid product, the phosphate content reduced to 1.6 wt% while the aqueous product after acid treatment contained dissolved calcium and phosphate. The pH of the aqueous fraction was adjusted with 1N NaOH, forming precipitate of phosphorus and confirmed to be $CaHPO_4$ using XRD (Yanagida et al., 2009). Other forms of calcium phosphate and $CaHPO_4$ can be widely used in agriculture, food industries and pharmaceutical industries. On the other hand, the aqueous product contained 8230 mg/L NH_3-N. Nitrogen was mainly recovered as dried ammonium sulphate ($(NH_4)_2SO_4$) precipitate by adding 1M H_2SO_4 corresponding to half of the nitrogen present in the SCWG aqueous product. Nitrogen recovery was about 92.9% and the purity of the precipitate was identified as 90.1% using XRD and the remaining 9.9% may most likely be potassium compounds as it is the second most abundant element in the feedstock (Yanagida et al., 2008). Potassium and ammonium sulphate are commonly used for fertilisers production, its recovery is important in agriculture (Yanagida et al., 2009). Treatment of SCWG aqueous product by any other means will make the process uneconomical.

- **Direct recovery from waste feedstock via the ‘quick wash’ process**

Thermal conversion methods such as pyrolysis, supercritical water gasification, hydrothermal liquefaction and hydrothermal carbonisation can produce by-products which are rich in recoverable phosphorus (Yanagida et al., 2009; Libra et al., 2011;Szogi et al., 2015), the chars are unattractive as sources of balanced nutrients (N:P) for use in crop production due to total or partial loss of nitrogen during thermal conversion (Szogi et al., 2015). In order to improve this nutrient balance, Szogi et al., developed the ‘quick wash’ process in manure byproducts as an alternative (Szogi et al., 2008). As shown in **Figure 2-8**, the ‘quick wash’ process involved rapid wet extraction of phosphorus from the raw solid manure using organic and mineral acids and the recovery of phosphorus in a concentrated solid form by the addition of lime and an organic polymer forming calcium phosphate precipitate ($Ca_3(PO_4)_2$). By washing with acid, large amounts of phosphorus in the form of organically bound phosphorus is converted to soluble phosphorus by rapid hydrolysis while phosphorus in insoluble inorganic phosphate complexes is also solubilized. Soluble phosphorus in supernant contains both inorganic-P and organic-P. Total soluble phosphorus is the sum of reactive-P and soluble unreactive-P. For colorimetric determination of phosphorus, soluble unreactive-P contain both organic forms and condensed forms of P as polyphosphates while the reactive-P consists of inorganic-P and loosely bound organic forms which were released during hydrolysis (Haygarth and Edwards, 2000). Both hydrolysis and solubilization of phosphorus can be obtained with mineral acids (such as sulfuric and hydrochloric), organic acids (such as malic, oxalic, citric etc) or a mixture of both organic acid and mineral acid. Precipitation of phosphorus in the liquid extract is achieved between pH 9-11 by adding an alkaline earth base to form alkaline earth metal-containing P compounds while an organic flocculant is added to enhance the preipitated P product.

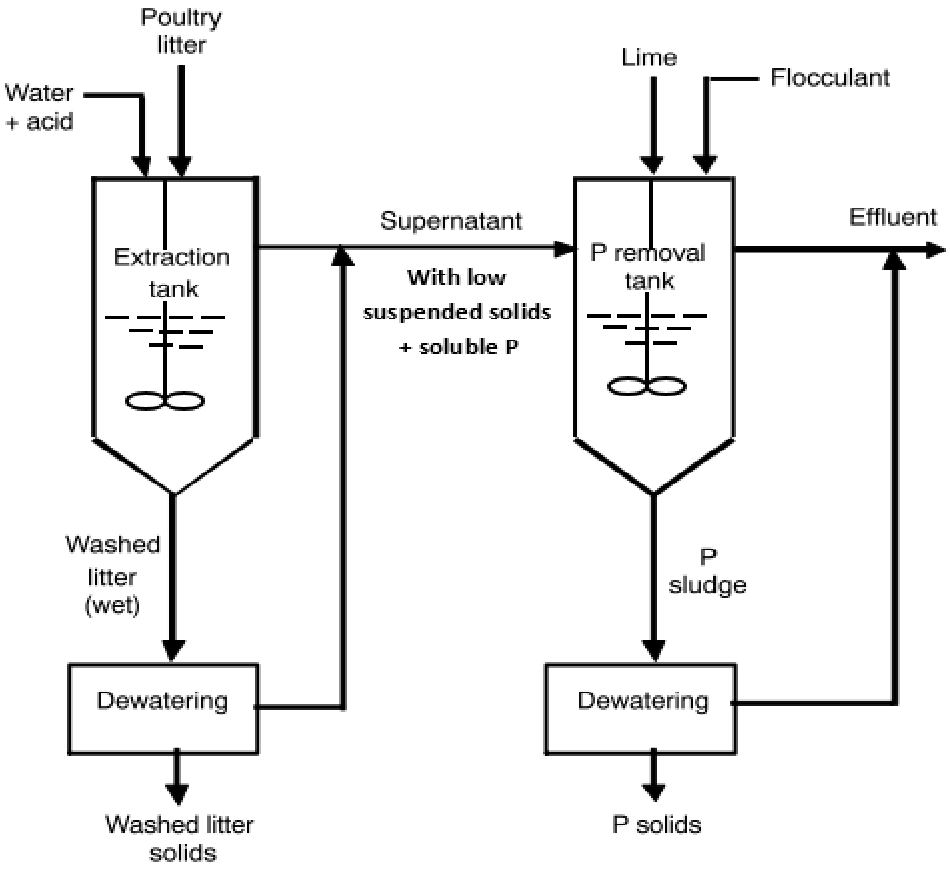


Figure 2-8: Schematic diagram showing manure ‘quick wash’ process

(Szogi et al., 2008)

After the process, the concentrated phosphate is about 15% of the large volume of manure which could be transported easily and used as an effective fertiliser. They concluded that the ‘washed’ residue has an optimal N:P ratio which is suitable for use in crop growth and safe for land application. Also the liquid effluent after precipitation could be recycled into the treatment system or used on cropland as a liquid fertiliser. The ‘quick wash’ process is conducted at ambient temperature, therefore there is no loss of organic carbon or nitrogen compared to the other thermal conversion methods. During acid extraction of pig manure to recover phosphorus, inorganic –P is released by dissolution of Ca, Mg and Al phosphates while organic –P is released by hydrolyzing phytate and other monoester –P compounds (Ajiboye et al., 2007; Pagliari and Laboski, 2012).

The technical feasibility of the quick wash process was evaluated by Szögi et al., (2015). Selective extraction of phosphorus was performed using increasing concentrations of both citric acid and hydrochloric acid (HCl) 2.5, 5, 10, 20, 40 and 80 mmol L^{-1}. They observed that 90% of the intial total phosphorus present in the pig manure was extracted with 20 mmol L^{-1} (pH 3.2) while 82% was extracted with 5 mmol L^{-1} (pH 4.7) which implies that total phosphorus extraction increased with increasing acid concentration. In contrast, extraction with de-ionised water was only 49%.

It was also observed that at similar concentrations, citric acid extracted more phosphorus than HCl. For instance citric acid at 10 mmol L^{-1} extracted 87 % while with HCl, 75% extraction was achieved. Although at higher concentrations of 20 mmol L^{-1} with pH < 3, more intense acidification was achieved with HCl than with citric acid (Szogi et al., 2015). HCl extracted more phosphorus (about 88%) at 40 mmol L^{-1} having pH 1.8 which is very corrosive and unnecessary oxidation of organic compounds could occur. Extraction of phosphorus with organic acid is a less corrosive and rate effective option during the quick wash treatment. Nitrogen was less efficiently extracted (37-49%) during the quick wash compared to phosphorus resulting in a significant amount of nitrogen remaning in the residue. It was concluded that the quick wash process reduces the agronomic phosphorus imbalance as the N:P ratio of the ‘washed’ residue is greatly increased compared to the unwashed feedstock.

Precipitation of phosphorus was conducted under alkaline conditions with and without a precipitation enhancer (polyacrylamide). The results showed indicated that TP concentrations decreased with increasing lime application rate. About 51% of TP was removed at pH 11 using 3.1g L^{-1} lime while TP was not removed in the control experiment with no lime addition having a pH of 4.5. Addition of 7 mg L^{-1} polyacrylamide to the lime experiments, significantly improved precipitation as pH between 8 and 9 was sufficient to precipitate 96 - 99% of the TP. At pH 8, about 12.8% P_2O_5 from the recovered precipitate was recovered compared to the low P_2O_5 content (5.4%) in the raw pig manure. The liquid after extraction contained significant quantities of organic –N , but less phosphorus. Volatilization of ammonia- N could occur during phosphorus recovery under alkaline conditions at ambient temperature and pressure (Szogi et al., 2006).

2.6.3.2 Physical recovery of phosphorus from wastewater

The presence of excess nitrogen and phosphorus in waste streams lead to eutrophication in surrounding surface water when discharged without treatment. Phosphorus rocks are important sources of fertiliser contributing largely to agriculture as well as industrial development (Z. Ye et al., 2014). In Europe, phosphorus recovery from wastewater using various technologies are operating on full or demonstration scale and have increased from 2 in year 1998 to 22 in year 2014 (Morse et al., 1998; Hukari et al., 2016). Struvite crystallisation has been implemented on full scale by AirPrex, Pearl and NuReSys while it has been demonstrated that Ecophos, Leachphos and ASH DEC are technically feasible (Hukari et al., 2016).

- **Filtration**

This method is used to remove particulate phosphorus i.e. all phosphorus compounds including both organic and inorganic which can be trapped on the filter (Rigler, 1973). Filtration is usually used at the primary stage when treating highly contaminated water with high particulate phosphorus (Lowe et al., 1992). Types of filtration systems include wetland filtration and sand filter.

2.6.3.3 Chemical recovery of phosphorus from wastewater

- **Precipitation**

Due to the scarcity of phosphorus rocks in many countries, recovery of phosphorus from wastewater and sludge anaerobic supernatant as struvite has gained importance as a promising source for phosphorus recycling (Gilbert, 2009). Struvite is a slow-release fertiliser which has low impurity levels compared to other phosphate fertilisers (Rahman et al., 2011).

The presence of excess nitrogen and phosphorus in waste streams lead to eutrophication in surrounding surface water when discharged without treatment. Phosphorus rocks are important sources of fertiliser contributing largely to agriculture as well as industrial development (Z. Ye et al., 2014).

The possibility of recovering struvite ($MgNH_4PO_4.6H_2O$) from farm, municipal and industrial waste streams has been demonstrated using pilot and full scale reactors in the laboratory recovering about 90% orthophosphate (Le Corre et al., 2007;Forrest et al., 2008). However this technology has not been widely adopted using these waste streams except for a few commercial units using urine and municipal sludge (Kataki et al., 2016). Recent research have focussed on improving the economics of the process by investigating alternative sources of recyclable magnesium and variety of seed materials.

- **Physical-chemical adsorption**

Recovery of phosphate and ammonium is an important aspect of environmental management as these species are present in varying concentrations in several wastewater (Battistoni et al., 2006;Ye et al., 2010;Song et al., 2011;Cai et al., 2013) and contribute to eutrophication in surrounding water bodies (Rittmann et al., 2011). Several ammonium and phosphate adsorbents have been identified. Some of which are pyrolysis solid by-products (biochars) and hydrochars recovered from hydrothermal processing in subcritical water. The application of biochars as adsorbents for wastewater contamination, gases and nutrients have been widely researched (Laird et al., 2010;Spokas et al., 2012; Zeng et al., 2013;Wang et al., 2015). These solid products are heterogeneous in nature consisting of inorganic matter, sorbed volatiles, nitrogen, sulphur and oxygen functional groups and organic matter (Spokas et al., 2012). Their biochar and hydrochar properties are usually linked to the composition of feedstock from which they were derived as well as the thermal conditions (Zhao et al., 2013; Wang et al., 2015).

The potential of nutrient adsorption using biochar or hydrochar is important to understand the behaviour and influence of these materials when they are added to compost, soil or any other high nutrient environment (Takaya et al., 2016a). Several studies have investigated the influence of physicochemical properties such as pH, cation exchange capacity, surface functionality and mineral content of a range of hydrochars and biochars derived from waste biomass. Char cation exchange capacity and surface chemistry are some of the factors which influence nutrient retention (Laird et al., 2010;B. Wang et al., 2015). For phosphate sorption, metal-phosphate precipitation re-actions played an important role (Zheng et al., 2010). Biochar phosphate adsorption capacity increases with increasing concentration of metal ions which is indicated with high ash content (Takaya et al., 2016a).

Takaya et al., (2016a) studied adsorption of phosphate and ammonium using biochar and hydrochar derived from a range of waste biomass. They observed that although these biochar or hydrochars had varying physicochemical properties due to the different processing conditions, the phosphate and ammonium sorption capacities were between 0-30mg g^{-1} and 105.8-146.4 mg g^{-1} respectively. They also reported that for surface area was not the most influential factor for ammonium adsorption while the presence of magnesium and calcium influenced phosphate sorption. Only a small fraction of phosphate (8.5 mg g^{-1}) and ammonium (<5 mg g^{-1}) was released.

Takaya et al., (2016b) investigated the enhancement of biochar mineral composition with chemicals such as acids, alkali and metal salts. They observed that phosphate uptake capacities of the biochars were significantly enhanced at low levels between 2.1-3.6% and higher levels between 66.4-70.3% with magnesium and concluded that mineral composition was a more influential factor than surface area.

2.6.3.4 Biological recovery of phosphorus from wastewater

- **Assimilation**

The role of microalgae in a wastewater treatment process is to assimilate nutrients and support bacteria with oxygen they give off during algal photosynthesis. Microalgae like other organisms needs phosphorus in the form of inorganic orthophosphate

($H_2PO_4^-$ or HPO_4^{2-}) through an active uptake process and it is used in its cell growth and metabolism (ATP) and a major component of nucleic acids, proteins and production of phospholipids (Becker, 1994). They are also capable of storing excess phosphorus sufficient for a prolonged growth in case there is limited phosphorus.

- **Enhanced biological phosphorus removal (EBPR)**

Enhanced biological phosphorus removal (EBPR) is a common feature of the wastewater treatment plant where organic substances are high and synthesize into heterotrophic biomass. As shown in **Figure 2-9**, phosphorus is consumed by a group pf heterotrophic bacteria requiring alternating aerobic and anaerobic conditions, adequate organic carbon such as volatile fatty acids and control of growth of glycogen accumulating organisms (Yuan et al., 2012). This method is inexpensive and environmentally sustainable, however there are challenges pertaining to stability and reliability (Oehmen et al., 2007). The phosphorus-rich sludge is discharged either by incineration introducing an additional disposal cost or used as feedstock in the anaerobic digestion process (Kodera et al., 2013). Another limitation is that for high organic load waste streams, energy recovery must be done in an anaerobic system (Rittmann, 2008).

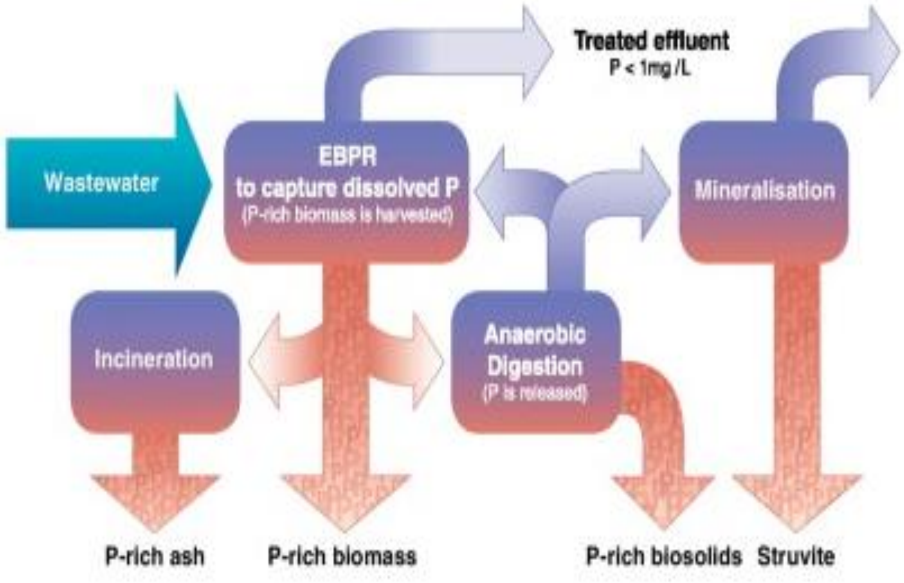


Figure 2-9: The EBPR process and the fate of by-products (Kodera et al., 2013)

2.7 Summary of Knowledge gaps

Management of wet wastes such as manures and sewage sludge in an environmentally sustainable way has been an increased environmental concern as these wastes are generated in huge quantities and have foul odour due to high degradation, emit greenhouse gases on decomposition and contain high pathogen load. These wastes contain high amounts of nutrients, therefore application on agricultural land as fertiliser is a traditional approach which causes pollution of surface and ground water during runoffs leading to eutrophication and hypoxia in water bodies.

Hydrothermal processing is identified as a potential conversion route for recycling nutrients from nutrient-rich wastes in addition to energy generation. However most research on this process have focussed on utilising wastes such as sewage sludge and a variety of biomass for energy but to a lesser extent manures. Other studies were on energy densification, optimization of process conditions such as temperature, residence time, feed: solid ratio for the production of useful by-products. Knowledge in the aspect of nutrient recycling from this process is limited. A number of studies gave an insight on nutrient concentration in either the solid product or aqueous waste stream while a few considered utilizing these aqueous waste streams for microalgae cultivation to obtain biomass to be used in biofuel production.

Although research on some aspects of nutrient recycling has been conducted, no study compares low-temperature and high temperature processes in terms of feedstock behaviour, yields, nutrient distribution, metal distribution, or evaluates potential routes for N and P recycling, enhancement of nutrient extraction with additives and recovery of phosphorus from aqueous waste streams other than biological recovery with microalgae.

Chapter 3 Materials and Methods

3.1 Introduction

This chapter presents a description of feedstocks used in this study and their origin, desciption of equipment used, experimental set up and process conditions, detailed description of experimental procedure and the various analytical techniques employed while carrying out this research. **Figure 3-1** shows the concept of this research in a clear and concise manner. This shows the various hydrothermal processing routes that were investigated, the various biomass samples used, the potential routes for nutrient release from the different biomass and the potential routes for recovery of these nutrients into useful products.

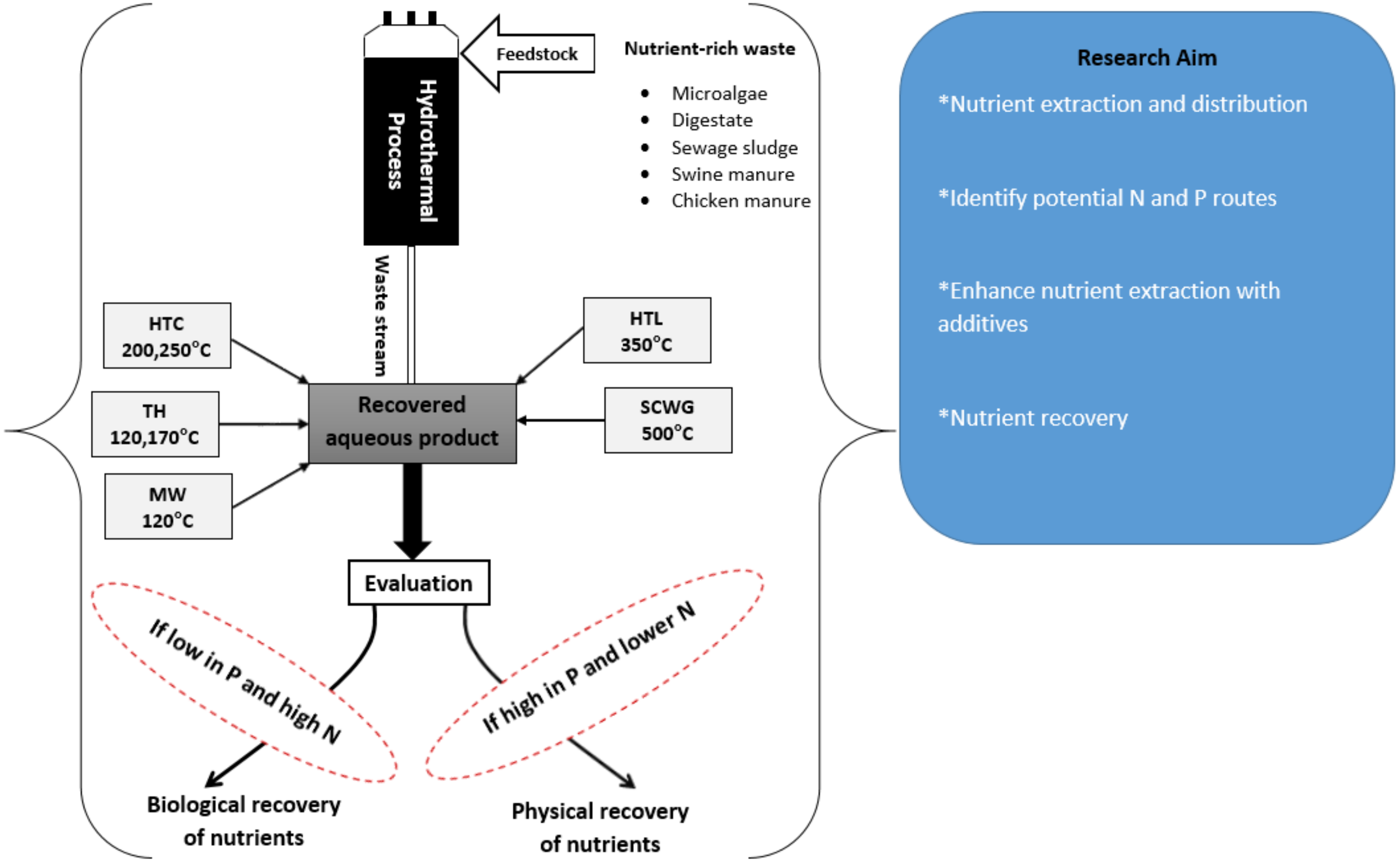


Figure 3-1: Flow chart showing the concept of the research work presented in this report.

3.2 Sample collection and preparation

Manure samples from poultry and swine were collected from the Leeds University farm. The samples were pre-dried at 60°C in an oven for several days in the farm laboratory. The digestate is a by-product of the anaerobic digestion of sewage sludge and provided by OWS (Belgium). It was also pre-dried at 60°C on site before being transported. Sewage sludge was obtained as a secondary sludge from Dewsbury wastewater treatment plant and dried at 60°C in an oven. The microalgae, *Chlorella vulgaris* was purchased in a powdery form from a commercial source (China). The seaweeds, *L.digitata*, *Saccharina* and *Alaria esculenta* were supplied by the Scottish Association of Marine Sciences (SAMS) and sampled from Clachan Sound, Scotland and then dried at 60°C in an oven.

All samples were dried for easy handling in the laboratory as wet samples are susceptible to high degradation with characteristic odour. In order to maintain uniform samples throughout this research, large batch of samples were collected and preserving them for the duration of the research entails drying. Finally the samples were dried for accountability purposes when carrying out a mass balance of nutrients and metals after hydrothermal processing. As it was part of the objectives of this research.

The manure, digestate and the sewage sludge samples were ground into powder using an Agate disc mill capable of grinding 150g of sample in a batch. After grinding, the samples were mixed thoroughly prior to sample characterisation and sample slurry preparation for use as feedstock in the hydrothermal processing reactor or microwave quartz vessel. For each batch of sample, it was thoroughly mixed and divided into four portions. Two out of the four portions were discarded while the remaining two portions were mixed and divided into four portions again. This was repeated in this manner until the sample was small enough for characterisation or the required quantity to prepare sample slurry was obtained. The ground samples were characterised (as stated in **Section 3.5**) without sieving. These samples were used as the feedstock for the various hydrothermal processes described in the following sections.

In order to create enough steam headspace for pressure build up so it does not exceed the tolerable pressure, specific sample slurry concentrations were used in the Parr reactor during thermal hydrolysis, HTC, HTL and SCWG according to the reactor specifications and microwave specifications. Also previous hydrothermal processing trials with higher solid loading in the Parr reactor, showed low conversion of the biomass samples.

3.3 Hydrothermal processing of biomass

3.3.1 Microwave Technology

Hydrothermal microwave extraction of the biomass feedstocks was performed in two batches. In the first batch of experiment, digestate, sewage sludge, swine manure, chicken manure and microalgae (*C. vulgaris)* were processed individually in a sealed quartz reaction vessel of 45mL volume in a 1.2kW Milestone StartSynth microwave oven (Milestone Srl, Italy). In all vessels, sample slurries were made up using 1g of feedstock in 15mL of de-ionised water (i.e. 15:1 water: solid ratio) and stirred using a glass rod. The samples were heated to 120°C within 3 minutes and the temperature was then kept constant for 15 minutes after which an in-built fan was operated to cool the samples. All experiments were performed in duplicate and the average results are reported in **Chapter 7.**

In the second batch of experiment, swine manure was processed in a similar fashion to that used above but in a range of different reagents. In addition to de-ionised water representing standard conditions, slurries of biomass were prepared in solutions of 0.1M Sodium hydroxide- NaOH, 0.1M Sulphuric acid- H_2SO_4, 0.1M Formic acid- HCOOH and 0.1M Acetic acid - CH_3COOH in the quartz vessels, each vessel containing one of the reagents. Sample slurries were made using the same water: solid ratio as stated above and stirred using a glass rod. All experiments were performed in duplicate and run using the same microwave heating programme. The results are reported in **Chapter 7**.

After microwave extraction, samples were cooled to room temperature with an in-built fan system. The contents of each quartz vessel was emptied into a pre-weighed 50mL centrifuge tube (**T_1**) and centrifuged for 15 minutes at 4000 rpm in order to separate the solid product from the aqueous product. The pH of the aqueous product was measured and then the aqueous product was decanted into a volumetric flask using a funnel. It was further diluted to 100 mL with de-ionised water. The diluted aqueous product was analysed for reactive phosphate (RP), total phosphorus (TP), ammoniacal nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN), total organic carbon (TOC) and metals. The procedures for these analyses are outlined in **Section 3.5.2**. The solid product (residue) left in the centrifuge tube was freeze dried for 48 hours after which it was weighed as **T_2**. The dried solid was characterised for proximate and ultimate analyses and metal analysis following extraction in nitric acid. The procedures for these analyses are outlined in **Section 3.5.1**.

3.3.2 Thermal Hydrolysis

Thermal hydrolysis was conducted at two different temperatures, 120°C and 170°C. Thermal hydrolysis of *C.vulgaris*, digestate, swine manure and chicken manure reported in **Chapter 4** were conducted at 170°C using a 75mL batch Parr reactor (Parr, USA). Slurries were made with each feedstock by using 3g of each feedstock mixed with 27mL of de-ionised water (i.e. 9:1 water: solid ratio) and stirred using a spatula.

Thermal hydrolysis of swine manure reported in **Chapter 5** and **Chapter 6** was conducted at 120°C and 170°C in a 600mL batch Parr reactor (Parr, USA) described in **Section 3.4**. The reactor was charged with 24g of swine manure and 220mL of de-ionised water to represent standard conditions and also in the presence of reagents including solutions of 0.1M Sodium hydroxide- NaOH, 0.1M Sulphuric acid- H_2SO_4, 0.1M Formic acid- HCOOH and 0.1M Acetic acid - CH_3COOH.

Both reactors are unstirred bomb type vessels made from stainless steel. Thermal hydrolysis was performed at a residence time of 1 hour in both reactors. The residence time was taken from the point the reactor reached the desired temperature. The heating rate in the 75mL reactor was typically between 9 and 13°C min^{-1} while in the 600mL reactor it was 10°C min^{-1}. The pressure during this process was typically between 0 to 0.1 MPa during thermal hydrolysis at 120°C while it was between 0.5 to 0.7 MPa during thermal hydrolysis at 170°C for both reactors. After 1 hour, the reactor heater was turned off and the reactor was allowed to cool to room temperature. After cooling, the pressure in the reactor was recorded and used to estimate the amount of gas produced. The contents of the reactor were emptied into a centrifuge tube and centrifuged for 15 minutes at 4000 rpm in order to separate the solid product from the aqueous product. This was performed as the viscous nature of the liquid results in difficulty with direct filtration. After centrifuging, the aqueous product was filtered through a pre-weighed Whatman filter paper (**F_1**) using a vacuum filter. The pH of the filtrate was measured before dilution with de-ionised water. Any solid residue remaining in the reactor were removed by rinsing with a further 10mL of de-ionised water for the 75mL reactor and a further 80mL of de-ionised water for the 600mL reactor and filtered through the same filter paper. After filtration, the residue was allowed to dry in the fume hood for 48 hours. The aqueous product was diluted with de-ionised water to a final volume of 50mL for aqueous product recovered from the 75mL reactor and 500mL for the aqueous product recovered from the 600mL reactor. Dichloromethane was used to extract any biocrude (tars and oils) from the walls of the reactor (if any). It was poured into a pre-weighed beaker (**B_1**) and allowed to evaporate. After evaporation, the weight of beaker was recorded as **B_2**. Although little or no biocrude is produced during thermal hydrolysis, rinsing the reactor with dichloromethane was performed to ensure uniformity in the procedure for biocrude extraction. The weight of the filter paper with dried residue was recorded as **F_2** and stored in a sample bag. The mass of solid product recovered was calculated as the difference between **F_1** and **F_2** while the mass of biocrude produced was calculated as the difference between **B_1** and **B_2**.

3.3.3 Hydrothermal carbonisation (HTC)

Hydrothermal carbonisation was conducted at two different temperatures 200°C and 250°C. Hydrothermal carbonisation of *C.vulgaris*, digestate, swine manure and chicken manure reported in **Chapter 4** was conducted at 250°C using a 75mL batch Parr reactor (Parr, USA). Slurries were made with each feedstock by using 3g of each feedstock mixed with 27mL of de-ionised water (i.e. 9:1 water: solid ratio) and stirred using a spatula.

Hydrothermal carbonisation of swine manure reported in **Chapter 5** and **Chapter 6** was conducted at 200°C and 250°C in a 600mL batch Parr reactor (Parr, USA), charged with 24g of swine manure and 220mL of de-ionised water to represent standard conditions and also with different solutions of 0.1M Sodium hydroxide- NaOH, 0.1M Sulphuric acid- H_2SO_4, 0.1M Formic acid- HCOOH and 0.1M Acetic acid - CH_3COOH which were used as reagents with varying pH. The same reactors that were used for thermal hydrolysis were also used during hydrothermal carbonisation. It was performed with similar water: solid ratio and at a similar residence time, having the same heating rate as stated in the **Section 3.3.2**. The residence time was taken from the point the reactor reached the desired temperature. The pressure during this process was typically between 3.4 - 4 MPa at 250°C in the 75mL reactor. In the 600mL reactor, the pressure was typically 1.4 MPa at 200°C and 4 MPa at 250°C.

After 1 hour, the reactor heater was turned off and the reactor was allowed to cool to room temperature. After cooling, the pressure of the reactor was recorded and used to estimate the quantity of gas produced. In this case, the contents of the reactor were separated by direct vacuum filtration through a pre-weighed Whatman filter paper (**F_1**). The pH of the filtrate was measured before dilution with de-ionised water. The solid residue left in the 75mL reactor was rinsed with 10mL of de-ionised water while the solid residue left in the 600mL reactor was rinsed with 80mL of de-ionised water. The rinsed residue was filtered through the same filter paper. After filtration, the filter paper containing the residue was allowed to dry in the fume hood for 48 hours. The aqueous product was diluted with de-ionised water to a final volume of 50mL for aqueous product recovered from the 75mL reactor or 500mL for aqueous product recovered from the 600mL reactor. As significant biocrude was produced during the HTC process, dichloromethane was used to extract biocrude from the walls of the reactor. It was poured into a pre-weighed beaker (**B_1**) and allowed to evaporate. After evaporation, the weight of beaker was recorded as **B_2**. The weight of the filter paper with dried residue was recorded as **F_2** and stored in a sample bag. The mass of solid product (hydrochar) recovered was calculated as the difference between **F_1** and **F_2** while the mass of biocrude produced was calculated as the difference between **B_1** and **B_2**.

Separation of the products after HTC of *C.vulgaris* in the 75mL reactor was slightly different due to the large amount of biocrude generated which made the residue sticky. Prior to this, 5mL of aqueous product was decanted from the reactor and collected in a glass bottle allowing the pH to be measured following which it was transferred back into the reactor. The complete content of the reactor was transferred into a separating funnel and combined with de-ionised water used to rinse the reactor. The reactor was also rinsed with 15mL dichloromethane to extract any biocrude on the wall of the reactor. This was also poured into the separating funnel which was shaken gently to ensure thorough mixing. After shaking, the separating funnel was left to stand for 30 minutes to allow for the separation of the distinct layers of the bio-crude, solid residue and the aqueous product. The biocrude was collected first through a pre-weighed Whatman filter paper (**F_a**) into a pre-weighed beaker (**B_1**) which was left to evaporate. The weight of biocrude recovered after evaporation was recorded as **B_2**. The aqueous product was collected next through another pre-weighed Whatman filter paper (**F_1**) into a volumetric flask. The distillation flask was rinsed with a little de-ionised water. The aqueous product was made up to a final volume of 50mL with de-ionised water while the weight of the filter papers after drying was recorded as **F_b** and **F_2** respectively and stored in a sample bag.

3.3.4 Hydrothermal liquefaction (HTL)

Hydrothermal liquefaction of *C.vulgaris*, digestate, swine manure and chicken manure reported in **Chapter 4** was conducted at 350°C using a 75mL batch Parr reactor (Parr, USA). Slurries were made with each feedstock by using 3g of each feedstock mixed with 27mL of de-ionised water (i.e. 9:1 water: solid ratio) and stirred using a spatula.

The same reactor used for thermal hydrolysis experiments was also used for hydrothermal liquefaction. It was performed with similar water: solid ratio and at a similar residence time, having the same heating rate as stated in the **Section 3.3.2**. The residence time was taken from the point the reactor reached the desired temperature. The pressure during this process was typically between 17 - 18.8 MPa depending on the feedstock. After 1 hour, the reactor heater was turned off and the reactor was allowed to cool to room temperature. After cooling, the pressure of the reactor was recorded.

Due to the large amounts of biocrude generated after HTL of each feedstock, dichloromethane was used to separate the products as the residue recovered was sticky in nature. Prior to this, 5mL of aqueous product was decanted from the reactor and collected in a glass bottle and used to measure the pH following which it was it was transferred back into the reactor. The complete content of the reactor was transferred into a separating funnel and combined with de-ionised water used to rinse the reactor. The reactor was also rinsed with 15mL dichloromethane to extract any biocrude on the wall of the reactor. This was also poured into the separating funnel which was shaken gently to ensure thorough mixing. After shaking, the separating funnel was left to stand for 30 minutes to allow for the separation of the distinct layers of the bio-crude, solid residue and the aqueous product. The biocrude was collected first through a pre-weighed Whatman filter paper (**F_a**) into a pre-weighed beaker (**B_1**). The dichloromethane in the beaker was allowed to evaporate and the weight was recorded as **B_2**. The aqueous product was collected next through another pre-weighed Whatman filter paper (**F_1**) into a volumetric flask. The distillation flask was rinsed with little de-ionised water and emptied into the filter paper as well. The aqueous product was made up to a final volume of 50mL with de-ionised water. The filter papers containing the residue were allowed to dry in the fume hood for 48 hours and the weights after drying were recorded as $\mathbf{F_b}$ and $\mathbf{F_2}$ respectively and stored in a sample bag.

The mass of solid product recovered was calculated as ($\mathbf{F_2}$-$\mathbf{F_1}$) + ($\mathbf{F_b}$-$\mathbf{F_a}$) while the mass of biocrude produced was calculated as the difference between $\mathbf{B_1}$ and $\mathbf{B_2}$.

3.3.5 Supercritical water gasification (SCWG)

Supercritical water gasification (SCWG) of *C.vulgaris*, digestate, swine manure and chicken manure reported in **Chapter 4** was performed at 500°C using a 75mL batch Parr reactor (Parr, USA) described below in **Section 3.4**. For this process, lower feedstock concentrations were used compared to thermal hydrolysis, HTC or HTL as previous research have shown that higher gasification efficiencies are achieved with lesser feedstock producing more H_2 gas and less CO or CO_2 (Chakinala et al., 2010;Muangrat et al., 2011). Slurries were made with each feedstock by using 1g of each feedstock mixed with 15mL of de-ionised water (i.e. 15 : 1 water: solid ratio) and stirred using a spatula. In addition, SCWG of two seaweed species: *Saccharina* and *Alaria esculentia* were performed in duplicate; one with heterogeneous catalyst 5% Ru/Al_2O_3 (Ruthenium Alumina catalyst) denoted by **'C'** and the other without catalyst denoted by **'NC'**. These experiments were performed primarily to determine the effect of catalyst on H_2 gas production during the SCWG process. The study by Cherad et al., (2013) presents the results on gas yields. However in this report, the gas yields from these experiments are not presented as it is beyond the scope of this objective. For the purpose of this work, only the aqueous products were characterized using the analytical techniques detailed in **Section 3.5.2**. Afterwards, these waste streams were used as culture medium for biological nutrient recovery discussed in **Chapter 8**.

The residence time for all SCWG experiments was 30 minutes at a pressure between 22 to 28 MPa depending on the feedstock being processed. The residence time was taken from the point the reactor reached the desired temperature. After 30 minutes, the reactor heater was turned off and the reactor was allowed to cool to room temperature. The pressure of the cool reactor was recorded and the gas generated was collected under pressure and analysed (gas composition results not included). The contents of the reactor were separated by direct vacuum filtration through a pre-weighed Whatman filter paper (**F_1**). The pH of the filtrate was measured before dilution with de-ionised water. The solid residue left in the reactor was rinsed with 10mL of de-ionised water and filtered through the same filter paper. After filtration, the filter paper containing the residue was allowed to dry in the fume hood for 48 hours. The aqueous product was made up with de-ionised water to a final volume of 50mL. Dichloromethane was used to extract any biocrude from the walls of the reactor (if any). Although very little biocrude is produced during SCWG, rinsing the reactor with dichloromethane was performed to ensure uniformity with biocrude extraction with other hydrothermal processes investigated. This was poured into a pre-weighed beaker (**B_1**) and allowed to evaporate. After evaporation, the weight of beaker was recorded as **B_2**. The weight of the filter paper with dried residue was recorded as **F_2** and stored in a sample bag.

3.3.6 Calculation of product yields

During the hydrothermal processes described above, a combination of the solid, aqueous, biocrude and gas products were generated. However depending on the processing temperature and the initial feedstock used, the quantities of these products recovered varied.

The solid yields (%) were calculated as follows:

$$Microwave\ extraction = \frac{T2 - T1}{Mass\ of\ feedstock\ used} \times 100 \qquad Equation\ 1$$

$$Thermal\ hydrolysis = \frac{F2 - F1}{Mass\ of\ feedstock\ used} \times 100 \qquad Equation\ 2$$

$$HTC = \frac{F2 - F1}{Mass\ of\ feedstock\ used} \times 100 \qquad Equation\ 3$$

$$HTC\ (C. vulgaris) = \frac{(Fb - Fa)\ + (F2 - F1)}{Mass\ of\ feedstock\ used} \times 100 \qquad Equation\ 4$$

$$HTL = \frac{(Fb - Fa)\ + (F2 - F1)}{Mass\ of\ feedstock\ used} \times 100 \qquad Equation\ 5$$

$$SCWG = \frac{F2 - F1}{Mass\ of\ feedstock\ used} \times 100 \qquad Equation\ 6$$

The biocrude yields from thermal hydrolysis, HTC, HTL and SCWG were calculated as:

$$\frac{B2 - B1}{Mass\ of\ feedstock\ used} \times 100 \qquad Equation\ 7$$

Previous studies have shown that the composition of gas from HTC and HTL processes was mainly CO_2 from HTC and HTL and none from thermal hydrolysis while H_2 was the main gas after SCWG (Biller and Ross, 2011;Cherad et al., 2013). The gas yields reported in **Chapter 4** were calculated using the ideal gas equation $PV = nRT$.

Where P = Pressure

V = Volume of reactor head space (0.048L for the 75mL reactor)

n = Number of moles

R = Molar gas constant (0.08206 L atm K^{-1} mol^{-1})

T = Temperature of the cool reactor (Kelvin)

Ideal gas equation is based on the following assumptions; that gas particles have no volume and are not attracted to each other. As there are no 'ideal' gases but real gases, the ideal gas law is still useful as a good approximation of the behaviour of many gases under many conditions (Miller et al., 2009;Ebbing and Gammon, 2010). The ideal gas equation is mostly accurate for monoatomic gases low to moderate pressures and temperatures that are not too low.

$$Number\ of\ moles\ (CO2) = \frac{Mass\ of\ CO2}{Molar\ mass\ of\ CO2} \qquad Equation\ 8$$

$$Gas\ yield = \frac{Mass\ of\ CO2\ generated}{Mass\ of\ feedstock\ used} \times 100 \qquad Equation\ 9$$

The yield of soluble products from each hydrothermal process was calculated as:

$$100 - (solid\ yield\ \%) + (biocrude\ yield\ \%)\ + (gas\ yield\ \%) \qquad Equation\ 10$$

3.4 Reactor design

3.4.1 75 mL Thermal hydrolysis, HTC and HTL reactor

Thermal hydrolysis and HTC using this reactor (**Figure 3-2)** were conducted at 170°C with pressure between 0.4-0.7 MPa and 250°C with pressure between 2.5-4 MPa respectively. Liquefaction experiments were conducted at 350°C and a pressure of 18 MPa for 1 hour. The heating rate of this reactor is between 9 - 13°C min^{-1} while the cooling rate was about 6°C min^{-1}. The reactor is an unstirred bomb type (Parr, USA) which is made from stainless steel. After every experiment, the power was switched off and the furnace was removed to allow reactor cool to room temperature.

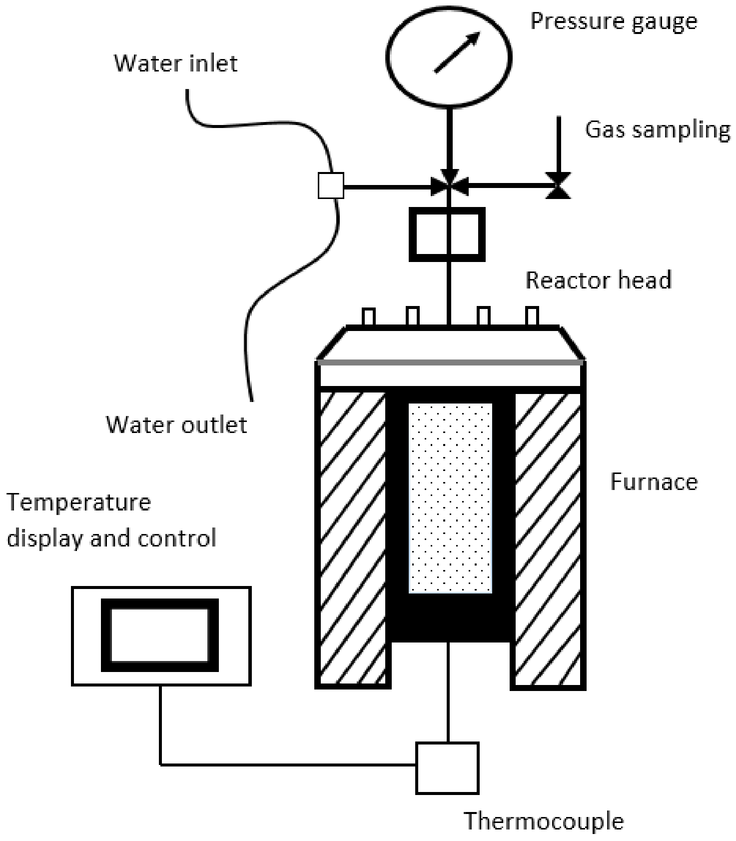


Figure 3-2: Layout of the 75 mL Reactor

The reactor head has a gasket to ensure proper sealing. A bursting disk is fitted also in the reactor as a safety device and releases the contents of the reactor when pressure in the reactor reaches 20MPa. Two thermocouples are fitted as well; one controls the temperature of the reactor while the other controls the temperature inside the reactor. The temperature display system shows only the temperature inside the reactor. The pressure is measured by a sensor and displays on the pressure gauge. A cooling system is installed as well to protect the reactor parts from high temperature. Results from experiments performed using this reactor are reported in **Chapter 4**.

3.4.2 600 mL Thermal hydrolysis and HTC reactor

Thermal hydrolysis experiments at 120-170°C and HTC experiments at 200-250°C reported in **Chapter 5** and **Chapter 6** were performed using the 600mL batch unstirred (Parr Instrument Co., Moline, Illinois, USA) shown in **Figure 3-3**. The reactor has a maximum operating temperature of 500°C and pressure of 35 MPa. Its inner diameter is 63.5 mm and has a wall thickness of 15.9 mm. This reactor is heated using a 3 kW ceramic heater and a J-type thermocouple (accuracy ± 1°C) which monitors the reactor temperature. The thermocouple is inserted into a thermowell on the reactor head which extends into the interior reaction chamber. The operating pressure was measured with the pressure gauge which is mounted on the reactor head. It is calibrated between 0-35 MPa (accuracy ± 0.05 MPa).

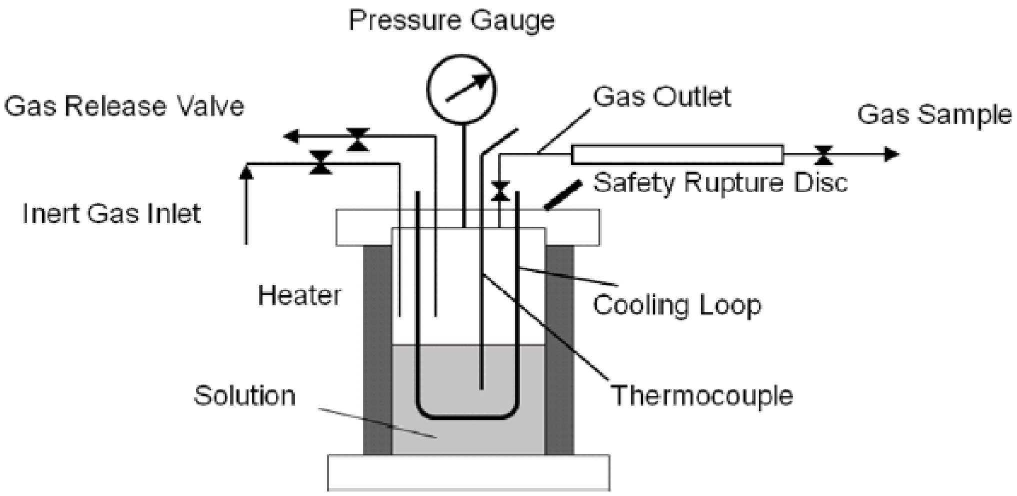


Figure 3-3: Layout of the 600 mL Reactor

The reactor is made up of two main parts; an upper part (reactor head) and a reaction chamber. The reactor head consists of a gas inlet valve which is mainly for introducing inert gases used for purging and a gas outlet valve used for gas sampling or to purge the reactor. It also has a safety bursting disk which is calibrated to 25 MPa. The volume of liquid used was 220 mL to avoid excessive pressure build up within the reactor.

3.4.3 SCWG reactor

SCWG experiments were performed in a small unstirred Inconel reactor (**Figure 3-4**) which was obtained from Parr Instrument Co., Moline, Illinois, USA. As gasification is conducted under severe process condition, Inconel reactors are used. The composition of the reactor material is different from the composition of the 75mL TH, HTC or HTL reactor as gasification is a more severe process than TH, HTC or HTL. The SCWG reactor is made from Nickel Chromium based super alloys - the strongest Ni alloy which have excellent resistance to oxidation and are corrosion proof.

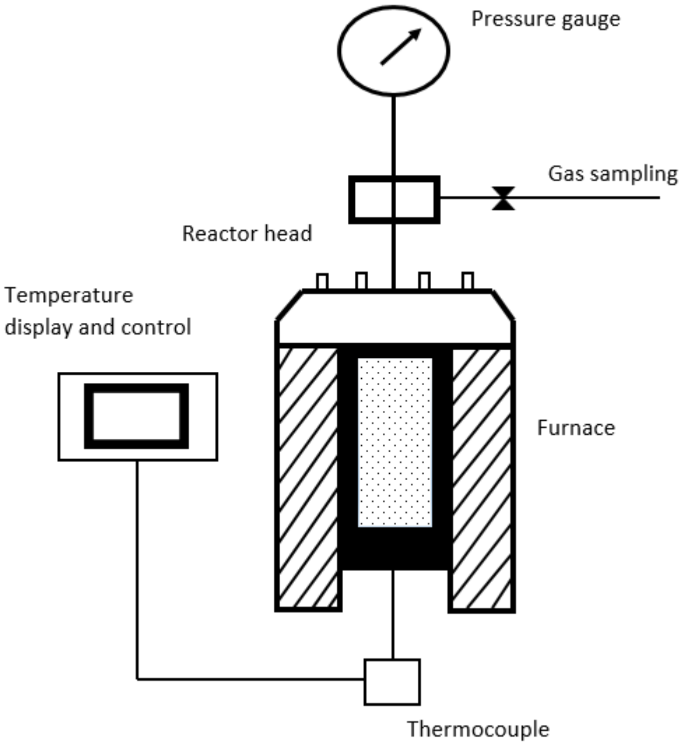


Figure 3-4: Layout of the SCWG reactor

The reactor has a volumetric capacity of 75mL with inner diameter 25mm and wall thickness 9.53 mm. Its maximum operating temperature and pressure is 600°C and 45 MPa respectively. The reactor is heated with a 1.5kW ceramic furnace which is equipped with a lever to manually shift it in a vertical direction. The reactor temperature is monitored with a J-type thermocouple with accuracy ± 1°C which is fitted in a thermowell at the bottom of the reactor. The thermocouple is connected to a temperature controller which has a digital monitor that displays the reactor temperature. The pressure gauge (accuracy ± 0.5bar) mounted on the reactor head measures the operating pressure. Also on the reactor head is a gas sampling unit which is fitted with high pressure valves. The maximum liquid in the reactor did not exceed 15 mL so as to prevent pressure build up according to the reactor specifications.

A safety rupture disc is fitted to the reactor. It is designed to rupture when the reactor pressure exceeds the safety pressure level. The maximum safe pressure for this reactor is 40 MPa which corresponds to about 500°C. The reactor was placed in a fume cupboard where all the experiments were carried out.

3.5 Characterization of feedstock and recovered products

3.5.1 Analysis of feedstock and solid residues

3.5.1.1 Proximate analysis

Proximate analysis of the various feedstocks; *Chlorella* vulgaris, *Laminaria digitata*, swine manure, chicken manure, OWS digestate and sewage sludge was performed using a Thermogravimetric analyser (TGA) to determine the moisture, volatiles, fixed carbon and ash contents in the unprocessed samples. Proximate analysis was also performed on all the solid products recovered from hydrothermal processing of these feedstocks. This was to determine any changes in the volatiles, fixed carbon and ash compared to the unprocessed feedstock which was used as a starting material for the hydrothermal process. **Figure 3-5** shows a typical TGA profile. The percentage compositions of each of these parameters were deduced from their individual TGA profiles. All measurements were repeated in duplicate and the mean values have been reported. The results are presented in **Chapter 4**, **Chapter 5** and **Chapter 7**.

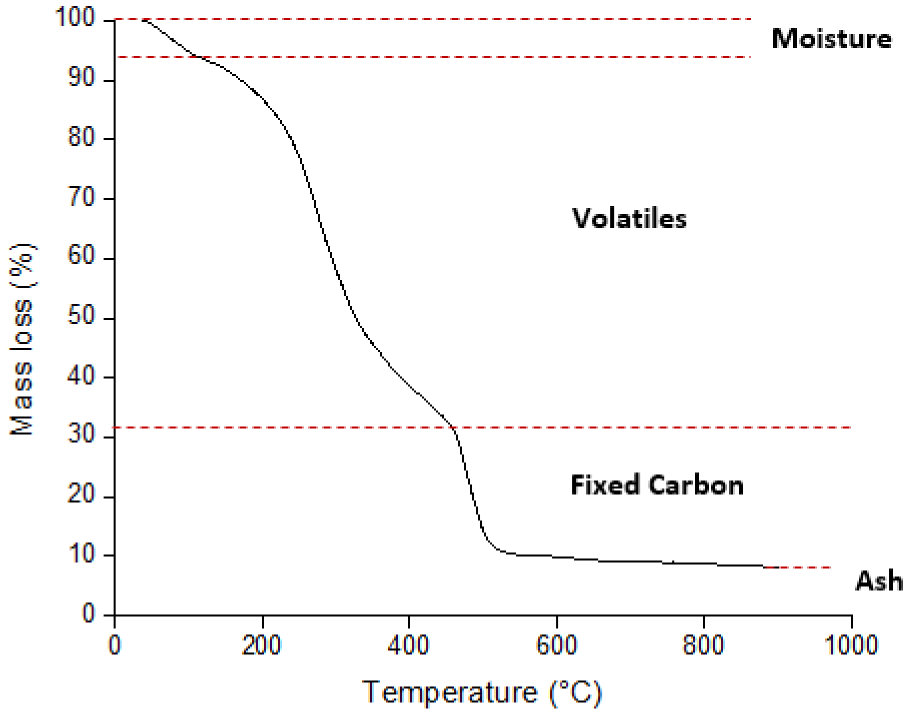


Figure 3-5: Typical TGA profile

3.5.1.2 Ultimate/ Elemental analysis

Ultimate analysis was performed using a CE Instruments Flash EA 1112 Series elemental analyser for all feedstocks investigated in this study as well as the recovered solid products from each hydrothermal process in order to determine the % composition of Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) contents. The analyser was calibrated with pure chemical standards such as BBOT, dl-Methionine, L-Cystine, Sulphanilamide and Atrophine. The typical compositions of these chemical standards are presented in **Appendix 1**. About 2.5mg of standards and samples (unprocessed feedstock and hydrochar) was placed in a tin capsule using a spatula and wrapped tightly to ensure there was no entrainment of air and contaminants which could result in a false detection of C, H, N, S. The wrapped samples were placed in a rack starting with the pure standards and a reference material such as oatmeal and coal (C, H, N, S content presented in **Appendix 1**) were placed after every ten sample duplicates to check for retention time drift. The reference materials used in this analysis matched the sample matrix. The samples were systematically flash combusted initially at 900°C. The composition of Oxygen (O) was determined by difference. The calculated calorific value of each feedstock and recovered solid product was based on the percentages of the C, H, N, S and O on a dry basis (db). All measurements were repeated in duplicate and the mean values have been reported. The results are presented in **Chapter 4**, **Chapter 5** and **Chapter 7**.

3.5.1.3 Metal analysis

Trace metal analysis of the various feedstocks and recovered solid products were carried out by digesting 200mg of sample with 10mL concentrated HNO_3 in a quartz vessel using a microwave digester. After cooling, the digested samples were diluted to a total volume of 50 mL using high purity water. Metals such as potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), iron (Fe) and aluminium (Al), nickel (Ni), cobalt (Co), copper (Cu), lead (Pb) and manganese (Mn) and zinc (Zn) were analysed using the inductively coupled plasma optical emission spectrometry (ICP-OES).

Phosphorus content in the digested unprocessed feedstocks and recovered solid products was analysed by colorimetry using the ascorbic acid method. Prior to the colorimetric test, 3mL of digested sample was diluted to 100mL. Colorimetric analysis was performed using 8mL of the diluted sample which was put in the Nessler tube and made up to 50mL (as stated in the procedure attached in **Appendix 3**).

3.5.2 Analysis of aqueous phase

3.5.2.1 pH

The aqueous product was recovered from the various hydrothermal processing routes by filtration using Whatman Type 3 filter papers (10 cm diameter) and a vacuum pump. Prior to pH measurement, the volume of aqueous product recovered was measured using a measuring cylinder as this is needed for mass-balance of nutrients and metals. The pH was measured using a pH meter calibrated at pH 4, pH 7 and pH 10 using appropriate pH buffer solutions. Duplicate pH measurements were taken for all samples.

3.5.2.2 Total Organic Carbon

The concentration of total carbon (TC) and inorganic carbon (IC) in the recovered aqueous products were determined using a Schimadzu TOC-5000 using the differential method. The total organic carbon (TOC) concentration in each aqueous product is reported as the difference between TC and IC concentrations. Duplicate measurements were taken for all samples and the mean concentrations have been reported in **Chapter 4**, **Chapter 5** and **Chapter 7**.

3.5.2.3 Total Kjeldahl Nitrogen and Ammoniacal – Nitrogen

The aqueous products were analysed for Total Kjeldahl Nitrogen (TKN) and ammoniacal nitrogen (NH_3-N). All samples were analysed in duplicate and the mean concentrations have been reported.

TKN determination starts with a digestion step which involved transferring 2mL of the aqueous product in a digestion tube and diluting to a final volume of 50 mL using de-ionised water. A blank containing 50mL of de-ionised water was also included in the digestion process. A copper catalyst tablet and a few glass beads were added to each tube using tongs. The tubes were placed in a rack and 10 mL concentrated sulphuric acid was added to each tube. The samples were allowed to boil briskly in a digester block with the scrubber switched on. This is a safety procedure as the scrubber traps the fumes produced during the digestion process. The digester block was turned off when the volume in the tubes had reduced greatly with a straw or greenish colour as an indication of complete digestion. The tubes were allowed to cool before the distillation step.

2mL of aqueous product was made up to 100mL with de-ionised water for NH_3-N determination. A blank containing 100mL of de-ionised water was also included.

Distillation for all NH_3-N and TKN samples starts with the blank tubes. The samples were distilled into 50 mL of boric acid solution in a Duran bottle placed under the receiving arm of the distiller. The appropriate program (either ammonia or TKN) is selected on the distiller menu. The protocol for NH_3-N and TKN determination is enclosed as **Appendix 3** for detailed information on reagent preparation and calculation.

3.5.2.4 Total phosphorus (TP) and reactive phosphate (PO_4^{3-}-P)

All aqueous samples were analysed for total phosphorus (TP) and reactive phosphate (PO_4^{3-}) using the ascorbic acid method by colorimetry. The samples were analysed in duplicate and the mean concentrations have been reported.

Analysis of total phosphorus concentration in the aqueous product required a pre-digestion step using the persulphate digestion method as shown in **Appendix 3**. The samples were digested using 100mL conical flasks as open vessel digestions. Each flask contained 0.4g solid ammonium persulphate with 2mL of each sample diluted to 75mL final volume and mixed thoroughly. A blank was also included in the digestion process containing 75mL of de-ionised water. One drop of phenolphthalein indicator solution was added to each flask following which, 1mL of 5.6M sulphuric acid solution was added. The flasks were placed on a pre-heated hot plate at 220°C to boil gently until it reached the 10mL mark. After digestion, the samples were left to cool and poured into a 100mL volumetric flask making up the volume with de-ionised water.

The colorimetric analysis uses a combined reagent which is freshly prepared and is stable for 4 hours. The recipe for the preparation of this reagent is enclosed in **Appendix 3**. The spectrophotometer was calibrated with 2.5, 5.0, 7.5 and 10mL of 5 mg P/L in a Nessler tube which corresponds to 0.25, 0.5, 0.75 and 1.0 mg P/L. A blank was included in the calibration which contained 50mL de-ionised water corresponding to 0 mg P/L. 8mL from the diluted digested aqueous sample was placed in a Nessler tube and made up to 50mL with de-ionised water. 8 mL of the combined reagent was added to each tube and the absorbance of the developed colour (for both the standard phosphate solution and the digested aqueous sample) was recorded after 10 minutes.

2mL of the undigested sample was diluted to 100mL prior to the colorimetry analysis. 8mL of diluted sample was placed in a Nessler tube and made up to 50 mL with de-ionised water. 8mL of the combined reagent was added to each tube and the absorbance of the developed colour was recorded after 10 minutes.

3.5.2.5 Metal Analysis

The recovered aqueous products from the various hydrothermal routes were analysed for metals. Metals such as potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), iron (Fe) and aluminium (Al), nickel (Ni), cobalt (Co), copper (Cu), lead (Pb) and manganese (Mn) and zinc (Zn) were analysed using the inductively coupled plasma optical emission spectrometry (ICP-OES).

3.6 Cultivation trials on biological nutrient recovery

3.6.1 Mass production of Stock Algal Culture

Stock culture of pure *Chlorella vulgaris* shown in **Figure 3-6** was purchased from the Culture Collection of Algae and Protozoa (CCAP), Scottish Association for Marine Science. It was used to inoculate three sterilized 2 litre vertical bioreactors containing Bold's Basal Medium (BBM) as shown in **Figure 3-7**. These reactors were constantly supplied with air using a small aquarium pump connected via a flow meter. The pure culture was mass produced in these bioreactors to provide viable inoculum for the cultivation trials and to reduce any risk of contamination. The pure stock culture was regularly maintained and used as inoculum for the growth trials when it reached exponential phase.

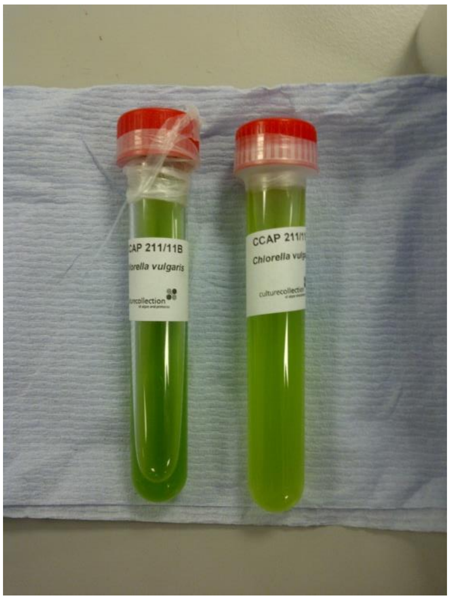


Figure 3-6: Purchased pure stock culture of *Chlorella vulgaris*

Figure 3-7: Mass production of *C.vulgaris* in Basal Bold media using vertical bioreactors

3.6.2 The Cultivation System

Cultivation trials were conducted in bioreactors using 500mL conical flask and the microcultivator**. Figure 3-8** and **Figure 3-9** show the typical set up of the bioreactors used for the cultivation trials.

Each 500mL bioreactor contained 200mL culture media and covered with a foam bung. The flasks were connected to an air supply tube as shown in **Figure 3-8** with air constantly supplied to each flask throughout the 14 days growth period to provide a source of CO_2 and agitation of the culture. The foam bung was used to prevent contamination of the culture from the external environment and to minimize evaporation losses. The setup was illuminated for 12 hours daily using fluorescent lamps which were placed approximately 40cm above the bioreactors.

Figure 3-8: 500mL bioreactors showing growth of *C. vulgaris* in various dilutions of the HTG process water from various feedstocks

The multicultivator MC 1000 (**Figure 3-9**) was used also for the cultivation trials. It is a very cost effective small scale device which has been developed for the cultivation of algae at the same time. The device consists of a power supply, control unit, optical density sensors, cultivation vessel, water pump, temperature sensor, water level sensor, main gas dispenser tube, air pump (located behind the control unit) and finally the cooling and heating unit. The cultivation vessel comprises of a water bath with its temperature regulated by the heating and cooling unit located at the right hand corner. High temperature of the water in the bath may arise from the high incident rays on each tube. There are 8 tubes immersed in the water bath. Each tube could contain 85mL of the growth media. Each compartment is separated with a plastic which demarcates each cultivation tube from the other and prevents light penetration from neighbouring compartments. The source of lightning for this device is the LED panel which is located at the back and supplies an array of white LEDs creating incident rays on each cultivation tube with maximum intensity of about 1000µmol.m^{-2}.s^{-2}. The light intensity in each tube can be adjusted separately using the menu in the control unit. Also, the lightning protocol for the growth trials was set in the control unit. The water pump automatically refills the water bath when it goes below the minimum level. The water level sensor sets off the alarm when the water level is low. The main gas dispenser tube bubbles gas to the individual gas inlets for each cultivation tube. The flow rate in each tube was adjusted separately using the control unit. During the 14 day growth trials, the device automatically measured the optical densities in the different cultivation tubes according the set protocol in the control unit.

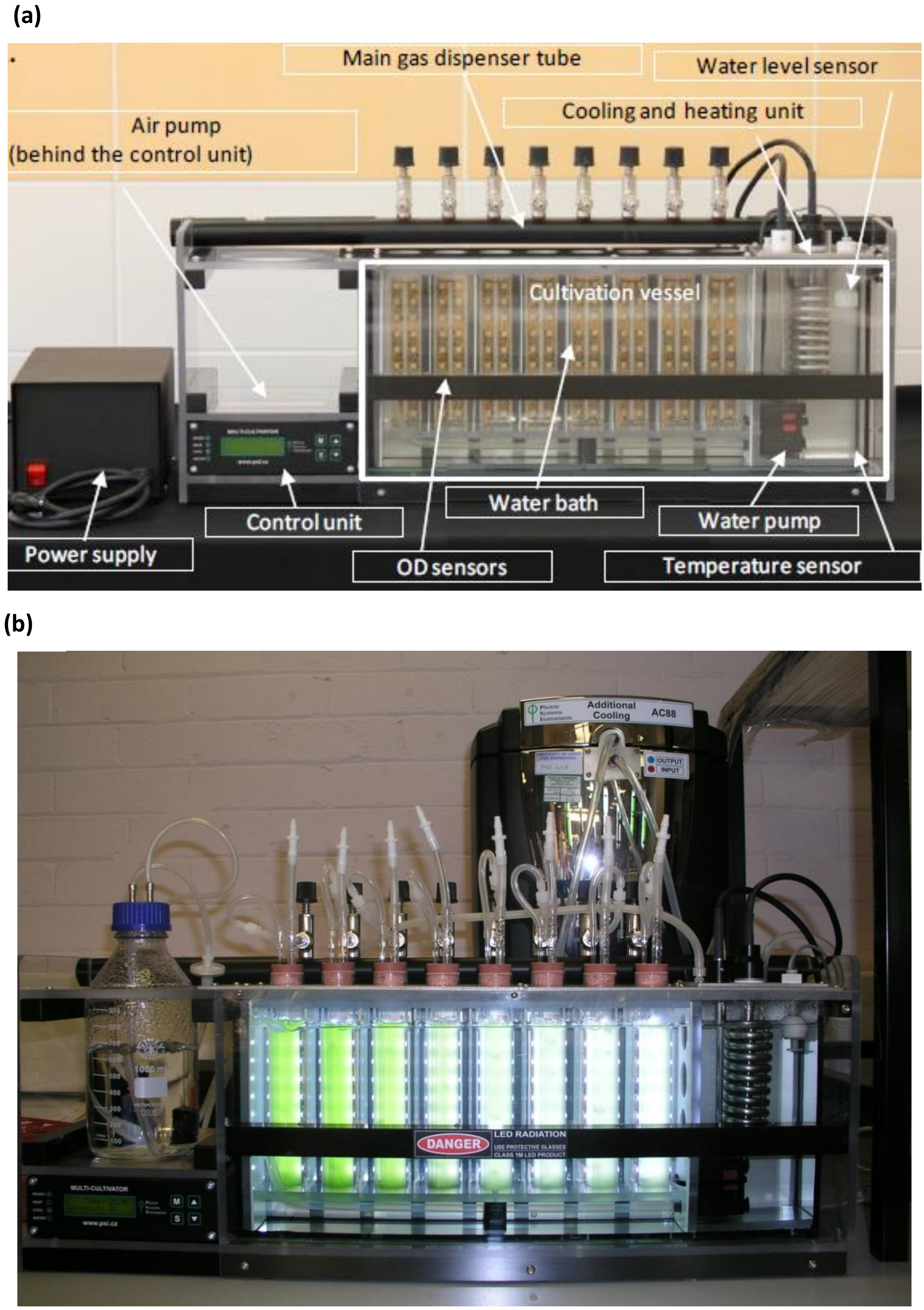


Figure 3-9: (a) Parts of a multicultivator (b) The multicultivator in use showing growth of *C.vulgaris* in various SCWG aqueous products

3.6.3 Cultivation Trials

Aqueous products from supercritical water gasification (SCWG) processes were generated to be used as culture media for the growth trials. The cultivation trials were carried using varying concentrations of these aqueous products to determine which dilutions favour the most algal growth.

Cultivation trials were conducted in several batches carried out one after the other. In the first batch, the aqueous products from catalysed and non-catalysed SCWG of *Saccharina* were used. The aqueous products were sterilized and each diluted to 1:50, 1:200 and 1:400. 200mL of these diluted samples was poured into a 500mL conical flask to be used as the culture media. The basal bold media was used as the control experiment. 20 mL of *C.vulgaris* culture at exponential phase from the vertical bioreactors (**Figure 3-7**) was used as inoculum in each flask. Duplicate experiments were performed using the same culture media but this time the microcultivator was used to compare the growth of *C.vulgaris* using these two cultivation systems.

Another set of cultivation trials was performed using aqueous products from SCWG of *Chlorella vulgaris*, sewage sludge and *Laminaria digitata*. These aqueous products were diluted to 1:50, 1:200 and 1:400 and 200mL of the diluted aqueous product was poured into 500mL conical flask. The same volume of inoculum as stated in the first batch was used for this batch. The basal bold media was used as the control experiment.

The growth rate in each of these 500mL bioreactors was monitored over a 14 day period using the analytical techniques described in **Section 3.6.4** during which they were expected to reach the stationary growth phase. The operating conditions for all growth trials conducted remained the same.

3.6.4 Analytical Techniques

One of the basic ways routinely used to evaluate the performance of microalgal cultivation systems is to estimate the biomass produced (Becker, 1994). The growth of microalgae is usually expressed in terms of an increase in biomass over a given period of time. Various analytical techniques used to determine the algal growth were turbidity, pH, total suspended solids (TSS) and volatile suspended solids (VSS).

3.6.4.1 Turbidity

Turbidity measurement is commonly used as it is a non-destructive procedure and results could be obtained quickly (Becker, 1994). It represents the concentration of suspended particles or cloudiness in a culture sample at a given wavelength causing light transmitted in one direction to scatter or be absorbed. Results obtained are expressed in Nephlometric Turbidity Units (NTU). 10mL of sample was taken each day to measure turbidity using the DR/890 HACH colorimeter. Before turbidity of any sample was measured, the colorimeter was calibrated using 10mL of de-ionised water as a blank.

3.6.4.2 pH

The pH of the culture was measured using a pH meter. The same sample collected for turbidity measurement was used. This test measures the degree of basicity or acidity of an algal culture medium. The pH meter was calibrated at pH 4 and pH 7 using buffer solutions before the pH of any sample was measured.

3.6.4.3 Total suspended solids and volatile suspended solids

Estimation of microalgal dry weight is only a direct way of determining the biomass produced. However, it is not the only method used for monitoring because it only depicts the physio-chemical state of the culture and does not differentiate between the suspended non-biological substances and the algal biomass itself (Becker, 1994).

The filter was prepared by first wetting it with distilled water and filtering using a vacuum pump. It was then placed in a crucible to be dried in the furnace at 550°C for

15 minutes to remove any volatile compounds or impurities that may be present. Afterwards, it was cooled in a desiccator and labelled appropriately before use.

15mL of sample was collected from a well-mixed bioreactor and filtered through an already weighed standard glass fibre filter using a vacuum pump until it was visibly dry. The filter together with the residue retained was then placed in an oven to dry at 70°C overnight. Afterwards, the sample was removed and placed in a desiccator to cool. The weight of the filter after drying was measured using a measuring scale and recorded for each sample. An increase in the weight of the fibre-filter shows the total amount of suspended algal solids in the collected sample. The dried residue samples from TSS was placed in a crucible and ignited in a furnace at 550°C for 1 hour. Afterwards, it was removed and cooled in a bell jar desiccator at room temperature.

The residual weight was measured and recorded. Volatile Suspended Solids (VSS) measures the organic fraction present in the algae sample and provides a more accurate measure of the amount of biomass produced than TSS (Becker, 1994). The loss in weight on ignition gives an approximate amount of organic fraction present in the solid sample represented as VSS. According to Eaton and Franson, (2005), TSS and VSS are calculated as follows:

$$TSS, \frac{Mg}{L} = \left((b - a) \times 1000\right) \div v \qquad Equation\ 11$$

$$VSS, \frac{Mg}{L} = \left((A - B) \times 1000\right) \div v \qquad Equation\ 12$$

Where:

v = volume of sample used, mL

a = weight of dry filter, mg

b = weight of dry filter and residue, mg

A = weight of residue + dish before ignition, mg

B= weight of residue + dish or filter after ignition, mg

3.7 Adsorption of phosphate for chemical recovery using modified biochar

The aqueous products from thermal hydrolysis and HTC using H_2SO_4 reported in **Chapter 5** had the highest total phosphate concentration compared to the other additives. These aqueous products were used for the phosphate adsorption experiments. The first set of adsorption was performed at varying concentrations of phosphate - 250mg/L, 500mg/L, 750mg/L and 1000mg/L using the aqueous product from 120°C, 170°C, 200°C and 250°C. The pH of these diluted samples was adjusted to 7 with 0.1M HCl and 0.1M NaOH. As the diluted samples were acidic, adjustment of pH using 0.1M NaOH resulted in a higher degree of dilution, making the set concentration of 250mg/L, 500mg/L, 750mg/L and 1000mg/L to deviate into a lower concentration of phosphate.

3.7.1 Adsorption using varying concentrations of aqueous products

20mL of these phosphate solutions were added to 40mg Mg-treated biochar in duplicate 50mL conical flasks. The flasks containing the samples were shaken in a water bath at 160rpm and 25°C for 24 hours. The initial phosphate concentrations used in this study was high and a representative of a typical aqueous product from hydrothermal processing of swine manure. The shaking speed, temperature and duration of adsorption were chosen based on the previous studies. The shaking speed used in this study (160rpm) is similar to the shaking speed used in the studies by Tian et al., (2009), Yan et al., (2010) and Kose and Kıvanc, (2011). The ratio of the adsorbent material to the phosphate solution was similar to the studies by Tian et al., (2009) and Carvalho et al., (2011). The duration of adsorption used was similar to the study by Freitas De Sousa et al., (2012). After 24 hours, the samples were filtered using a Whatman filter paper. The solid on the filter paper was left to dry for 48 hours while the filtrate was analysed for phosphate by colorimetry using the ascorbic acid method described in **Section 3.5.2**.

3.7.2 Adsorption at varying pH

In the second batch of adsorption experiments, the phosphate concentration with the highest phosphate removal in batch one was used. The results from batch one showed that more phosphate was adsorbed at lower concentrations. Therefore the 250mg/L phosphate solutions from 120°C, 170°C, 200°C and 250°C aqueous products were used. In this batch of experiment, the effect of pH was investigated. The phosphate solutions were prepared and pH adjusted to 8 and 9 using 10M NaOH and 0.1M HCl. Higher concentration of NaOH was used in this batch as the samples were highly acidic even after dilution. As observed in the first batch, using 0.1M for pH adjustment resulted in a higher degree of dilution.

20mL of these phosphate solutions were added to 40mg Mg-treated biochar in duplicate 50mL conical flasks. The flasks containing the samples were shaken in a water bath at 160rpm and 25°C for 24 hours. After 24 hours, the samples were filtered using a Whatman filter paper. The solid on the filter paper was left to dry for 48 hours while the filtrate was analysed for phosphate by colorimetry using the ascorbic acid method described in **Section 3.5.2**.

The results from batch one and batch two experiments are presented in **Chapter 8.**

3.7.3 Analysis of Mg-treated biochar and adsorbed biochars

The Mg-treated biochar and a selection of biochars recovered from batch one and batch two were analysed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The biochars selected were those from the experiments having the most phosphate adsorption. The SEM was conducted to determine the surface characteristics of these adsorbed biochars in comparison with the initial Mg-treated biochar. The images showed an indication of a precipitate. The EDS was conducted to determine the chemical composition of the precipitate formed on the adsorbed biochars in comparison with the composition of the Mg-treated biochar. The EDS peaks of the adsorbed biochar are indicative of the presence of calcium phosphate or struvite compound in the formed precipitate. SEM and EDS images from Mg-treated biochar, calcium phosphate standard, struvite standard and typical image of an adsorbed char are shown in **Chapter 8** while other SEM/EDS images are in **Appendix 3**.

Chapter 4 A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing

4.1 Introduction

In this chapter, four technologies namely thermal hydrolysis (HYD), hydrothermal carbonisation (HTC), hydrothermal liquefaction (HTL) and supercritical water gasification (SCWG) were studied at 170°C, 250°C, 350°C and 500°C respectively. Hydrothermal processing of these nutrient-rich feedstocks- *Chlorella vulgaris*, digestate, swine manure and chicken manure were performed at 60 minutes except for SCWG which was performed for 30 minutes.

Hydrothermal processing at different temperatures was performed as a comparative study to determine the behaviour of each feedstock with an increase in process temperature from 170°C to 500°C. The objectives of this experiment were to determine the effect of reaction conditions on product yields, aqueous and solid product composition, nitrogen extraction, phosphorus extraction, metal extraction, the distribution of these nutrients between the solid and aqueous products. The potential for recovery of these nutrients from each hydrothermal route is discussed in **Chapter 8**. Detailed methodology of the experimental setup and analytical methods used for both the solid and aqueous products are in **Chapter 3**.

4.2 Characterisation of feedstock

4.2.1 Proximate and ultimate analyses

The feedstocks used for the various hydrothermal processes were analysed for moisture, ash, volatiles and fixed carbon as well as the elemental composition as stated in **Chapter 3** and the results are shown in **Table 4-1**.

The proportion of ash in each feedstock is high. The swine manure, chicken manure and microalgae had similar levels of ash ranging from 9.8 to 12.7 wt. % while the digestate contained significantly higher ash levels about 61.2 wt. % respectively. Among the feedstocks, microalgae had the highest volatile content (82.7 wt.%) while significantly higher volatile content was present in the manure ranging from 61.1 to 62.7 wt. %. The digestate showed the lowest volatile content following anaerobic treatment.

The results show that nitrogen content was highest for the microalgae (*C. vulgaris*) at 9.7 wt. % followed by the chicken manure (5.7 wt. %), and swine manure (3.0 wt. %) with the digestate containing the least (2.7 wt. %). *C. vulgaris* is well known to be rich in protein which is responsible for its high nitrogen content (Toor et al., 2011). In all the four feedstocks investigated, the proportion of sulphur was less than 0.7%. The microalgae contained the highest carbon and hydrogen content at 46.8 wt. % and 6.9 wt. % respectively. The carbon and hydrogen content in the swine manure was similar to microalgae. Both the microalgae and manure contain lipids that increase the carbon and hydrogen content in the feedstock. The digestate on the other hand contained significantly lower levels of carbon (18.3 wt. %). This reduction in carbon is due to the high levels of ash in this feedstock following anaerobic treatment. **Table 4-1** also lists the higher heating values (HHV) of the feedstock based on the Dulong equation (Xu et al., 2012). The digestate has the lowest HHV (7.8 MJ kg^{-1}) while the microalgae has the highest (21.1 MJ kg^{-1}). The swine and chicken manures were similar at 19.2 MJ kg^{-1} and 18.3 MJ kg^{-1} respectively.

Table 4-1: Proximate and ultimate analyses of various feedstocks investigated

	Proximate analyses (%)				Ultimate analyses[a] (%)					
Biomass	Moisture	Ash [a]	Volatiles	Fixed carbon	C	H	N	S	O[b]	HHV (MJ kg^{-1})
Chlorella vulgaris	3.4	9.8	82.7	4.5	46.8	6.9	9.7	0.5	26.3	21.1
Digestate	2.9	61.2	34.4	3.3	18.3	2.9	2.7	0.3	14.6	7.8
Swine manure	5.3	12.7	61.1	21.6	46.4	6.3	3.0	0.2	31.4	19.2
Chicken manure	5.6	10.9	62.7	21.5	43.9	6.5	5.7	0.2	32.8	18.3

[a] dry basis

[b] Calculated as difference between sum of C,H,N,S, ash

4.2.2 Nutrients and metals present in the various feedstocks

Table 4-2 lists the nutrient and metal content of the four unprocessed biomass feedstocks. Phosphorus was found to be highest in the microalgae (22,580 mg kg^{-1}) and lowest in the chicken manure (12,870 mg kg^{-1}). The swine manure contained similar levels of phosphorus to the digestate (15,580-16,430 mg kg^{-1}). The manure samples contained higher calcium content compared to the microalgae and digestate with 16,810 mg kg^{-1} and 23,580 mg kg^{-1}, respectively. The highest levels of calcium were found in the swine manure (36,770 mg kg^{-1}) and the lowest levels are in the microalgae (16,810 mg kg^{-1}). Chicken manure has the highest levels of potassium with 20,300 mg kg^{-1} compared to 8,060 mg kg^{-1} found in the swine manure, 4,530 mg kg^{-1} in the microalgae and 4,140 mg kg^{-1} in the digestate. The digestate contained the highest levels of iron and aluminium with 30,910 mg kg^{-1} and 19,220 mg kg^{-1} respectively, which is significantly higher than the levels found in manure and microalgae feedstocks. The concentration of iron in swine and chicken manure was 1,040mg kg^{-1} and 420 mg kg^{-1} respectively while the concentration of aluminium was 640 mg kg^{-1} and 760 mg kg^{-1} respectively.

Table 4-2: Levels of nutrients and metals in the biomass investigated (dry basis)

	Concentration (mg kg^{-1})							
Biomass	P[a]	K[b]	Ca[b]	Mg[b]	Na[b]	Ni[b]	Fe[b]	Al[b]
Chlorella vulgaris	22,580	4,530	16,810	5,310	7,650	450	2,810	2,570
Digestate (old)	16,430	4,140	23,580	5,100	6,410	420	30,910	19,220
Swine manure	15,580	8,060	36,770	9,600	3,950	510	1,040	640
Chicken manure	12,870	20,300	24,300	6,510	3,670	200	420	760

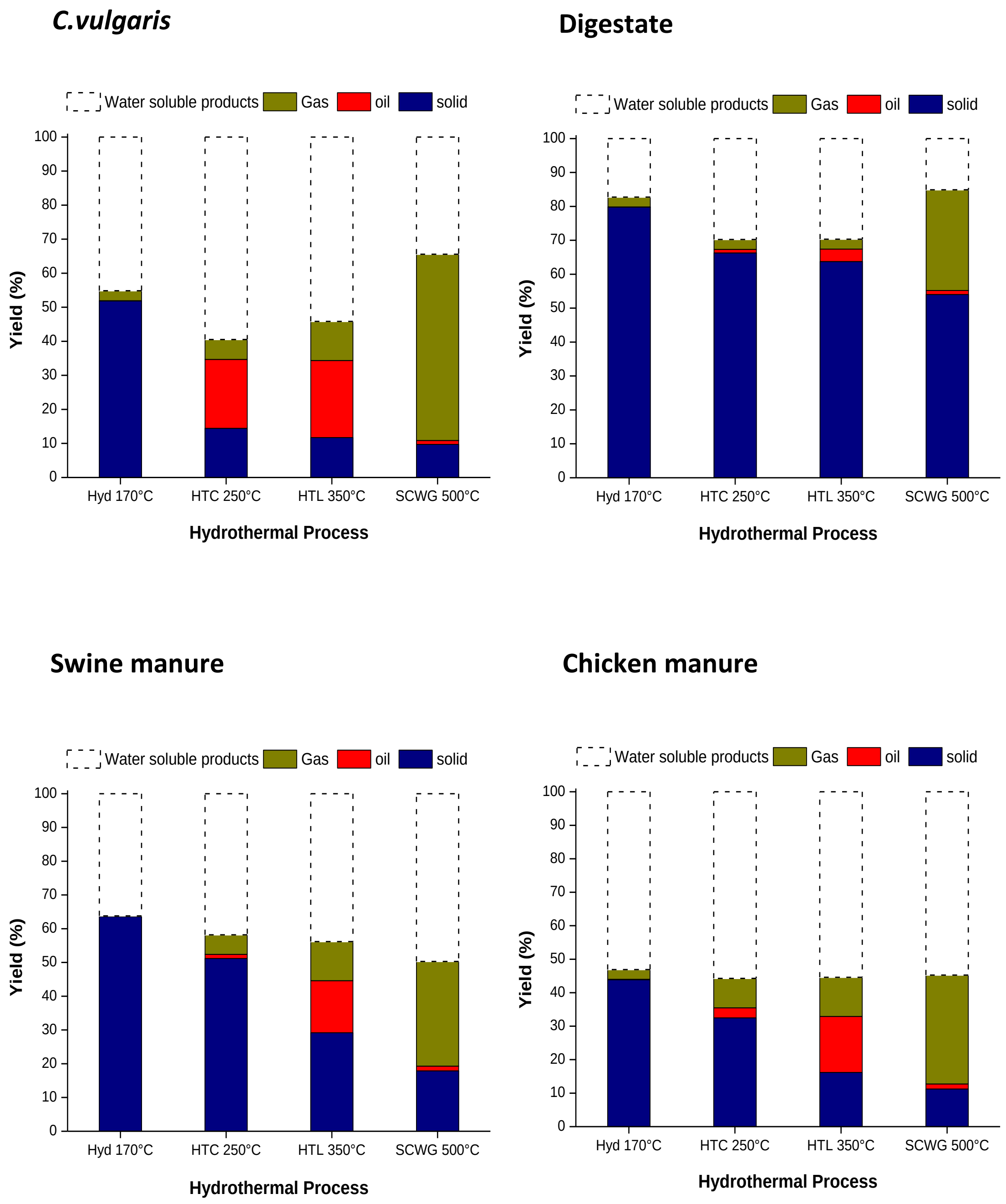
[a] Analysis by colorimetry
[b] Analysis by ICP-OES

4.3 Hydrothermal processing

4.3.1 Product yields

The product yields (i.e., solid, liquid, gas and oil) following hydrothermal processing of *C.vulgaris*, digestate, swine manure and chicken manure are shown in **Figure 4-1**. The product distribution is highly dependent upon process severity. The yields, residue formation, gas composition and the composition of the aqueous phase depend on the biomass being processed as well as the processing temperature (Toor et al., 2011). Among the various products obtained after hydrothermal processing, the residue and liquid phase contain most of the nutrients which were originally present in the unprocessed feedstock (D. López Barreiro et al., 2015).

In general, lower processing temperatures at 170°C and 250°C favour higher yields of solid residue compared to the higher processing temperatures at 350°C and 500°C. Thermal hydrolysis at 170°C typically produced the highest yields of solid residue for all the feedstocks. The highest levels of solid residue are observed for the digestate (80 wt. %) due to the high ash content, followed by the swine manure (64 wt. %), the microalgae (52 wt. %) and finally the chicken manure (44 wt. %). The digestate produces the highest yields of solid residue irrespective of process severity due to its high ash content. The levels of water soluble products generally increase with reaction severity and this is due to a combination of solubilisation of inorganics and increase in production of soluble organic hydrocarbons. The levels of syngas increase with reaction severity ranging from virtually no gas formation under thermal hydrolysis conditions to significant levels under supercritical water gasification conditions. Thermal hydrolysis at 170°C produces mainly solid residue and water soluble products. There are very few gaseous products and no oil formation after thermal hydrolysis for all the feedstock.



*oil refers to biocrude

Figure 4-1: Product yields from hydrothermal processing of various feedstocks

As shown in **Figure 4-1**, hydrothermal carbonisation at 250°C produces mainly residue and water soluble products with the exception of the microalgae, which contain a significant level of oil and so favours formation of bio-crude. The gas yield is more significant than in thermal hydrolysis and ranges from 6% to 12%. The digestate has once again the highest yield of residue (66 wt. %) due to its high ash content although some of the inorganics are also solubilised in the water phase. The swine manure has the second highest yield of residue (51 wt. %) followed by the chicken manure (33 wt. %) and the microalgae (14 wt. %). On further examination it was also observed that the hydrochar from the microalgae contains a significant level of oil (20 wt. %).

Hydrothermal liquefaction at 350°C begins to produce significant amounts of biocrude. The largest fraction is now the water phase which contains inorganics and soluble organic hydrocarbons. The levels of oil are highest for the microalgae (23 wt. %), the manures have a similar oil yield at 17 wt. % from chicken manure and 15 wt. % from swine manure while the digestate was much lower (4 wt. %). The reason for the high bio-crude yields exhibited by *Chlorella* is due to the high lipid content in its cell wall (Biller and Ross, 2011). The yields and characteristics of the bio-crude produced at this temperature depend largely on the biochemical composition of the unprocessed feedstock. Studies have shown that the bio-crude produced from HTL of microalgae have high heating values (Minowa et al., 1995; Biller and Ross, 2011; Jena et al., 2011). The bio-crude has a higher oxygen and nitrogen content than crude oil (Brown et al., 2010; Biller and Ross, 2011). Various studies have shown that the HHV of the bio-crude could be enhanced using heterogeneous catalysts (Duan and Savage, 2011). The gas produced during HTL is mainly CO_2 and the yields from all feedstock were relatively low compared to the yields from SCWG. About 12 wt. % of gas was produced from microalgae, swine manure and chicken manure whereas the digestate had the lowest gas yield of about 3 wt. %. Similar gas yields were observed by Biller et al., (2012) for HTL of microalgae. Supercritical water gasification at 500°C significantly increases the levels of gas produced although there is still considerable levels of polar organics dissolved in the water fraction as shown in **Table 4-7.** This indicates that gasification efficiency is low using these experiments however the general trend observed for the fate of inorganics, the main focus of this study, is unaffected. The highest gaseous fraction was observed for the microalgae (55 wt. %) although the other feedstocks produce similar levels ranging from 31 to 33 wt. %. The levels of residue were significantly lower than lower temperature processing and ranged from 10 to 15 wt. % for the microalgae and manure. The digestate produced once again the highest residue due to higher levels of ash.

4.3.2 Characterisation of the solid product

4.3.2.1 Proximate and ultimate analyses

Table 4-3 and **Table 4-4** lists the proximate and ultimate analysis of the residues produced from the different hydrothermal processes together with their higher heating value (HHV). The results indicate that the ash content in the solid product increases with reaction severity. The digestate is consistently higher and contains nearly 90 wt. % ash following SCWG. The volatile matter is significantly reduced with reaction severity producing a more carbonised solid product. The carbon content in the digestate and microalgae residue is reduced with increased severity whereas for the manures it remains relatively constant. The carbon content of the hydrochar recovered from the HTC of swine manure and chicken manure increases from 43-46 wt. % to 56 wt. % and 60 wt. % respectively. This has been observed previously as a consequence of dehydration and decarboxylation reactions (Falco et al., 2011). The levels of oxygen were lower in the solid products than in the unprocessed feedstock. The levels of nitrogen in the solid residue reduce with reaction severity for the microalgae, however for the manure there is still a significant level of nitrogen remaining in the residue after HTL and SCWG. Calculation of the heating values indicates that there is considerable energy in the solid product, particularly for the swine manure and chicken manure.

Table 4-3: Proximate, ultimate analyses and HHV of residues from microalgae and digestate

Conditions	Proximate analyses (%)				Ultimate analyses[a] (%)					
	Moisture	Ash [a]	Volatiles	Fixed carbon	C	H	N	S	O[b]	HHV (MJ kg^{-1})
C.vulgaris										
Hyd 170°C	3.5	13.0	70.6	13.4	50.8	6.8	7.3	0.5	21.7	23.1
HTC 250°C	4.1	50.3	39.1	8.5	30.7	4.1	4.2	0.2	10.5	14.4
HTL 350°C	2.0	76.8	19.8	2.9	15.1	2.1	1.8	0.1	4.1	7.3
SCWG 500°C	1.9	58.8	22.9	17.6	31.0	2.2	2.8	nd	5.3	12.7
Digestate										
Hyd 170°C	1.8	78.3	20.6	0.7	12.0	1.8	1.0	0.2	6.6	5.5
HTC 250°C	1.1	81.4	17.4	1.1	10.0	1.4	0.6	0.2	6.4	4.3
HTL 350°C	0.7	87.7	12.0	0.3	7.4	1.0	0.5	0.1	3.2	3.4
SCWG 500°C	0.9	89.0	10.5	0.5	5.6	0.7	0.5	0.1	4.2	2.1

[*] nd not detected

[a] dry basis

[b] Calculated as difference between sum of C,H,N,S, ash

Table 4-4: Proximate, ultimate analyses and HHV of residues from manure

Conditions	Proximate analyses (%)				Ultimate analyses[a] (%)					
	Moisture	Ash [a]	Volatiles	Fixed carbon	C	H	N	S	O[b]	HHV (MJ kg^{-1})
Swine manure										
Hyd 170°C	5.3	10.6	76.6	8.1	48.2	6.2	2.4	0.1	32.6	19.4
HTC 250°C	2.5	18.5	57.7	21.8	55.7	6.1	2.7	0.1	16.9	24.5
HTL 350°C	2.3	30.5	45.1	22.8	52.5	5.2	2.6	0.1	9.2	23.6
SCWG 500°C	1.4	40.4	18.6	40.2	49.7	2.7	2.3	nd	4.9	19.9
Chicken manure										
Hyd 170°C	3.4	10.7	72.5	13.7	50.1	6.7	3.6	nd	28.8	21.4
HTC 250°C	2.2	16.0	59.3	22.8	59.9	6.5	4.9	nd	12.6	27.4
HTL 350°C	1.9	29.4	45.7	23.6	54.7	5.6	3.9	nd	6.5	25.4
SCWG 500°C	4.1	41.8	19.2	36.7	48.9	3.0	3.1	nd	3.3	20.3

[*] nd not detected

[a] dry basis

[b] Calculated as difference between sum of C,H,N,S, ash

4.3.2.2 Nutrients and metals present in the residues

Table 4-5 and **Table 4-6** lists the levels of inorganics in the solid product following hydrothermal treatment and provides insight into the fate of the inorganics. When compared to the metals in the starting material as listed in **Table 4-2**, some general trends can be identified. The level of phosphorus in the residue increase with reaction severity. This is consistently observed for all feedstocks. A similar result was observed in the study reported by Zhu et al., (2011). They found that during SCWG of sewage sludge, most of the phosphorus is present in the solid residue. Yanagida et al., (2008) evaluated the behaviour of inorganics during SCWG of poultry manure. It was observed that most of the Ca, Si and P present in the unprocessed biomass are concentrated in the residue while nearly all the Cl, N and K in the unprocessed biomass was found in the aqueous product. Potassium is almost entirely extracted into the aqueous phase. A similar trend is observed for sodium although there is still some residual sodium remaining in the residues in this study. Calcium and magnesium on the other hand are concentrated in the solid residue; this is also observed for iron and aluminium. The solubility of phosphates during hydrothermal processing decreases in the presence of Ca due to precipitation of calcium phosphate (Dai et al., 2015). The level of nickel in the solid product following SCWG is particularly high. High levels of nickel have previously been observed in the process waters following SCWG and is a result of nickel leaching from the reactor walls (Lopez Barreiro et al., 2014). Supercritical water is corrosive and industrial application of SCWG is challenging as expensive alloys will be required (Toor et al., 2011).

Table 4-5: Nutrient and metal in the recovered residues from microalgae and digestate (dry basis)

Conditions	Concentration (mg kg^{-1})							
	P[a]	K[b]	Ca[b]	Mg[b]	Na[b]	Ni[b]	Fe[b]	Al[b]
C.vulgaris								
Hyd 170°C	21,240	250	26,060	7,650	3,650	140	6,190	4,850
HTC 250°C	93,100	1,740	98,280	33,860	5,360	240	14,090	16,540
HTL 350°C	157,200	15,610	146,250	48,140	10,900	240	27,010	23,880
SCWG 500°C	118,500	12,300	107,360	39,420	35,060	6,250	18,010	22,380
Digestate								
Hyd 170°C	17,210	2,650	24,660	6,400	4,520	230	35,260	20,270
HTC 250°C	19,330	3,030	28,140	7,050	3,930	240	38,770	22,890
HTL 350°C	19,340	3,490	29,340	7,710	4,390	240	40,280	23,770
SCWG 500°C	20,200	5,310	30,100	7,900	6,280	1,540	41,650	24,000

[a] Analysis by colorimetry
[b] Analysis by ICP-OES

Table 4-6: Nutrient and metal in the recovered residues from manure (dry basis)

Conditions	Concentration (mg kg^{-1})							
	P[a]	K[b]	Ca[b]	Mg[b]	Na[b]	Ni[b]	Fe[b]	Al[b]
Swine manure								
Hyd 170°C	15,490	220	39,950	5,890	5,050	110	1,580	1,350
HTC 250°C	29,610	190	55,900	9,820	5,150	120	2,220	1,660
HTL 350°C	39,470	230	81,070	20,540	5,230	200	3,690	2,300
SCWG 500°C	52,710	1,140	114,090	32,840	17,700	7,630	4,090	4,520
Chicken manure								
Hyd 170°C	14,030	200	35,410	4,510	4,980	120	1,270	1,650
HTC 250°C	24,490	350	47,780	11,260	5,620	110	1,510	1,970
HTL 350°C	40,230	740	61,740	19,040	6,758	130	2,120	2,090
SCWG 500°C	63,690	9,740	85,870	32,700	33,690	31,060	1,920	6,590

[a] Analysis by colorimetry
[b] Analysis by ICP-OES

4.3.3 Characterisation of the aqueous product

The aqueous products derived from each of the hydrothermal routes have been analysed quantitatively for each feedstock to determine the concentrations of nitrogen (N), phosphorus (P), total organic carbon (TOC) and other metals. The pH of the aqueous products was also monitored and the results are listed in **Table 4-7**.

4.3.3.1 pH

The pH of the aqueous phase recovered after reaction at the different conditions is shown in **Table 4-7** and results in a similar trend for each feedstock. Following thermal hydrolysis, the aqueous phase was acidic, ranging between pH 4.9 and 5.0, which becomes close to neutral under HTC conditions. As the process temperature increases to 350°C and beyond, the pH of the aqueous phase becomes basic ranging from between 8.2 and 8.8 after SCWG. At higher processing temperatures, there is an increased breakdown of nitrogen leading to the formation of ammonium and other alkaline products (Mumme et al., 2011; Cherad et al., 2013).

4.3.3.2 Total Organic Carbon (TOC)

The concentrations of TOC in the aqueous phase reduces with process severity as shown in **Table 4-7**. The TOC level in SCWG water phase was the lowest compared to HTL, HTC or thermal hydrolysis for all feedstock processed. The presence of organic carbon in the SCWG water phase implies that not all the organic content was converted to gas during the process. The addition of catalysts during SCWG has been shown to reduce the TOC levels of the aqueous product (Stucki et al., 2009). In this study, the highest levels of TOC were in the aqueous phase from hydrothermal processing of microalgae followed by the chicken manure, swine manure and digestate.

Table 4-7: pH, total organic carbon (TOC), nitrogen, phosphorus and potassium in the aqueous products

		Concentration (mg kg^{-1})			
Conditions	pH	TOC	Total N	Total P	Total K
C.vulgaris					
Hyd 170°C	5.0	196,870	47,960	8,510	4,850
HTC 250°C	7.1	179,120	60,390	8,370	3,820
HTL 350°C	8.3	94,640	62,040	6,450	2,850
SCWG 500°C	8.8	83,370	55,690	3,070	5,240
Digestate					
Hyd 170°C	5.1	65,740	19,560	1,360	2,330
HTC 250°C	7.7	62,350	18,610	840	2,340
HTL 350°C	8.2	46,980	17,110	560	2,040
SCWG 500°C	8.7	34,170	13,780	600	1,440
Swine manure					
Hyd 170°C	4.9	118,180	10,640	2,060	8,120
HTC 250°C	5.9	101,840	12,790	650	7,890
HTL 350°C	6.7	80,780	15,820	800	7,790
SCWG 500°C	8.2	44,510	19,970	710	6,050
Chicken manure					
Hyd 170°C	5.0	184,180	33,430	5,250	19,030
HTC 250°C	7.2	141,120	32,770	1,470	19,080
HTL 350°C	8.0	102,800	31,700	820	18,520
SCWG 500°C	8.5	48,670	34,300	1,060	12,600

4.3.3.3 Distribution of nitrogen

Hydrothermal processing at different temperatures affects the distribution of nitrogen. The total amount of nitrogen extracted into the aqueous phase following hydrothermal processing is shown in **Figure 4-2** and indicates that similar levels of total nitrogen (typically around 50 - 75 wt. %) are extracted from the chicken manure, microalgae and digestate at each of the processing conditions. The nitrogen extracted from the swine manure was lower after thermal hydrolysis but increased from 37% at 170°C to 55 - 70% under HTL (350°C) and SCWG (500°C) conditions. The effect of hydrothermal processing temperature (180 - 240°C) on the nutrient behaviour in sewage sludge was investigated by Sun et al., (2013). They concluded that at lower processing temperatures (180°C), nitrogen solubilisation, originating from the breakdown of proteins, increased from 42% to 51% when the holding time was increased from 30 to 60 min and reaction temperature plays a dominant role in nitrogen solubilisation into the aqueous phase.

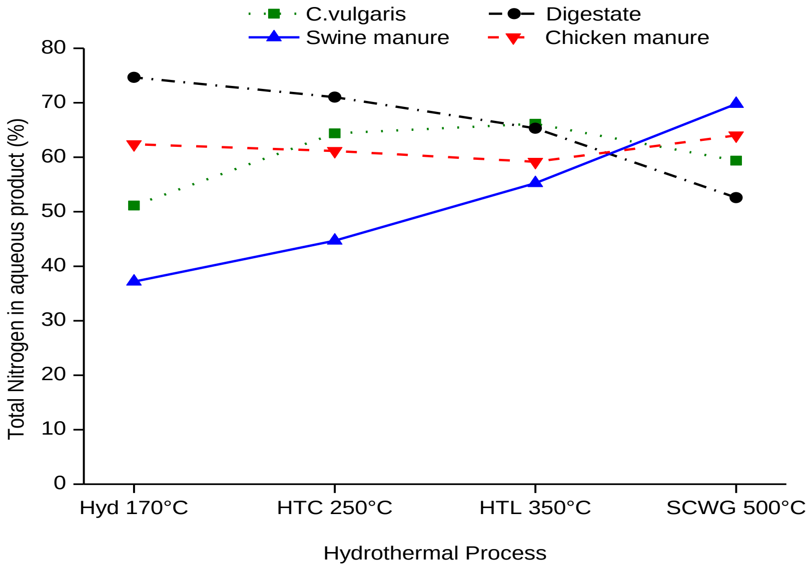
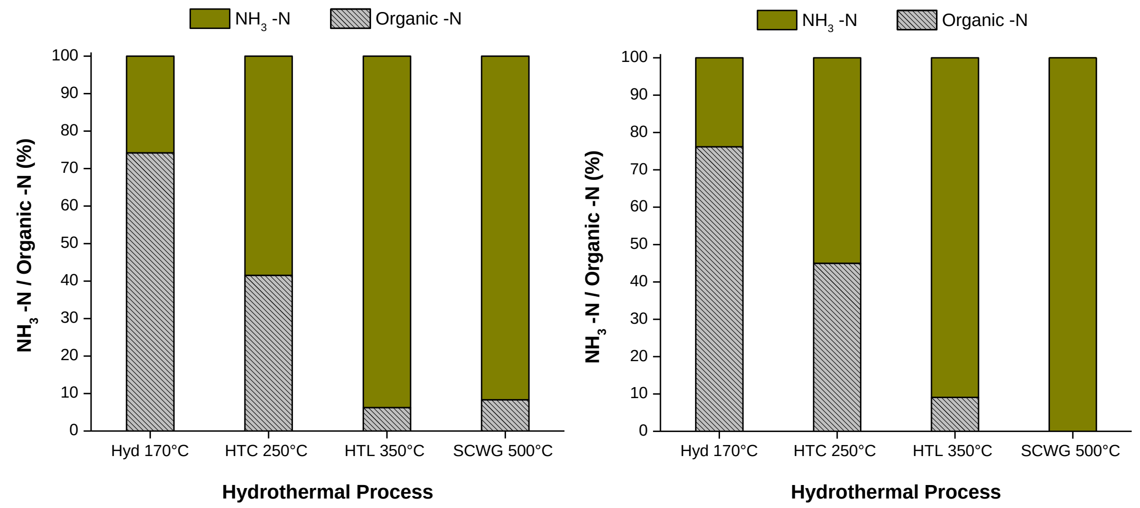


Figure 4-2: Extraction of total nitrogen into the aqueous phase

4.3.3.4 Forms of nitrogen present in the aqueous product

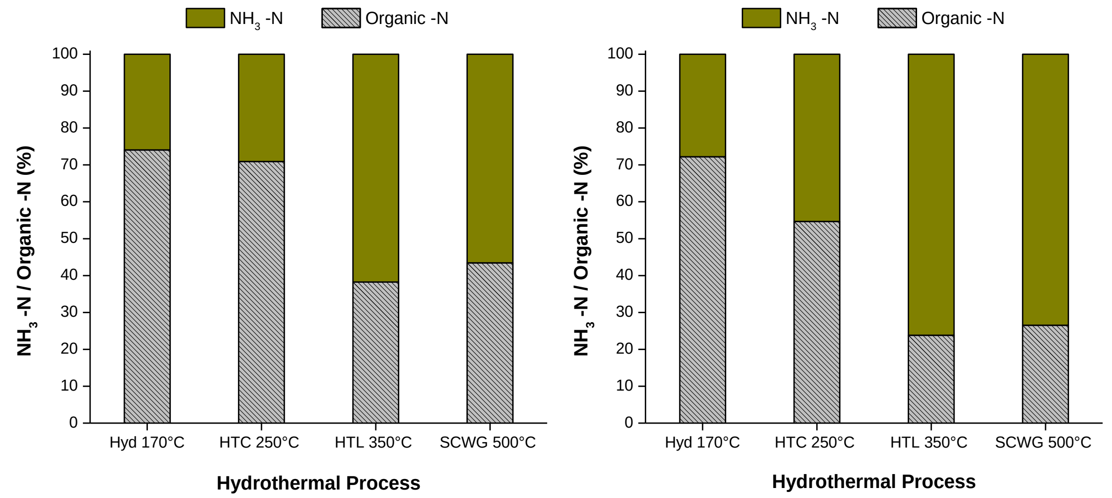
Figure 4-3 shows the distribution of organic- N and NH_3-N in the aqueous product for each feedstock at the different process severity. The levels of nitrogen in the form of NH_3-N significantly increase in the aqueous phase as process severity increases. This is similarly observed by Lu and Savage, (2015) during SCWG of a lipid-extracted hydrochar at 450 - 550°C. At 550°C, they achieved 90% nitrogen recovery as NH_3-N while at 600°C, 97.2% NH_3-N recovery was achieved. These graphs indicate that as the temperature reduces, more of the nitrogen is in the form of organic-N for each of the feedstock processed.

Organic-N is the dominant form in the water phase from lower processing temperatures (170 - 250°C). The results show that about 75% of the total nitrogen in the aqueous phase after thermal hydrolysis is organic. After HTC at 250°C, it reduces to about 40 - 70% and reduced further under HTL and SCWG conditions. The levels of organic-N for the microalgae and digestate were significantly lower (<10%) after HTL and SCWG whereas for the swine and chicken manure, there are still significant even at 350°C and 500°C. A similar trend was observed in the study reported by López Barreiro et al., (2015). They found that organic nitrogen in the HTL water phase degraded to ammonium after SCWG, increasing the fraction of ammonium compared to after HTL. In each hydrothermal process, similar levels of total nitrogen (TN) were observed in the aqueous phase for each feedstock. The microalgae had the highest levels of TN in the aqueous phase compared to the other feedstock due to higher levels of N in the feed.



C.vulgaris

Digestate



Swine manure

Chicken manure

Figure 4-3: Forms of nitrogen present in the aqueous products from various feedstocks

4.3.3.5 Distribution of phosphorus

Figure 4-4 shows the extraction of phosphorus into the aqueous phase for each of the different conditions. The results indicate that the extraction of phosphorus reduces with reaction severity. In this study, the aqueous phase from thermal hydrolysis has the highest levels of total phosphorus (TP) which reduces significantly as the process severity increases. At the lower temperatures, approximately 40% of the P was extracted from microalgae and chicken manure although the levels are lower for digestate and swine manure. The levels gradually reduce as the reaction severity increases to less than 15% under SCWG conditions.

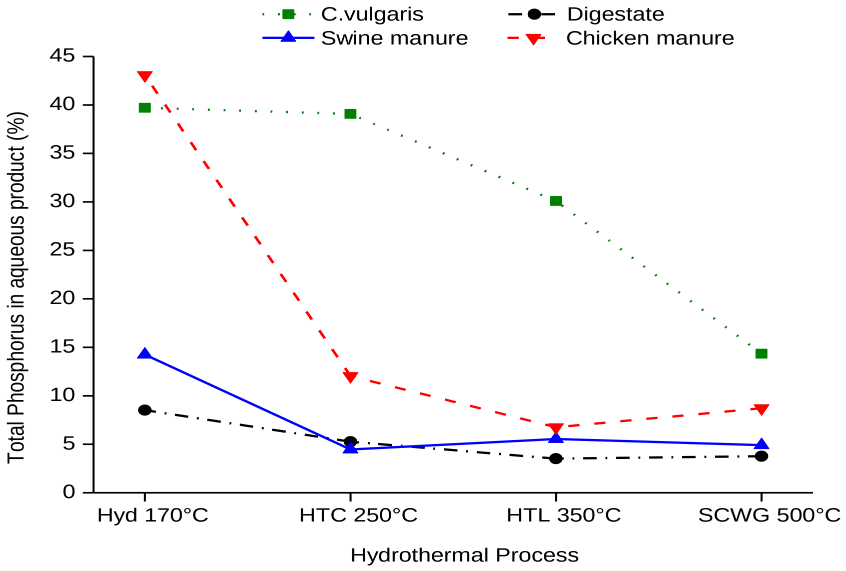


Figure 4-4: Extraction of total phosphorus into the aqueous phase

Further investigation of the aqueous products show that TP was made up of both organic and inorganic forms of phosphorus.

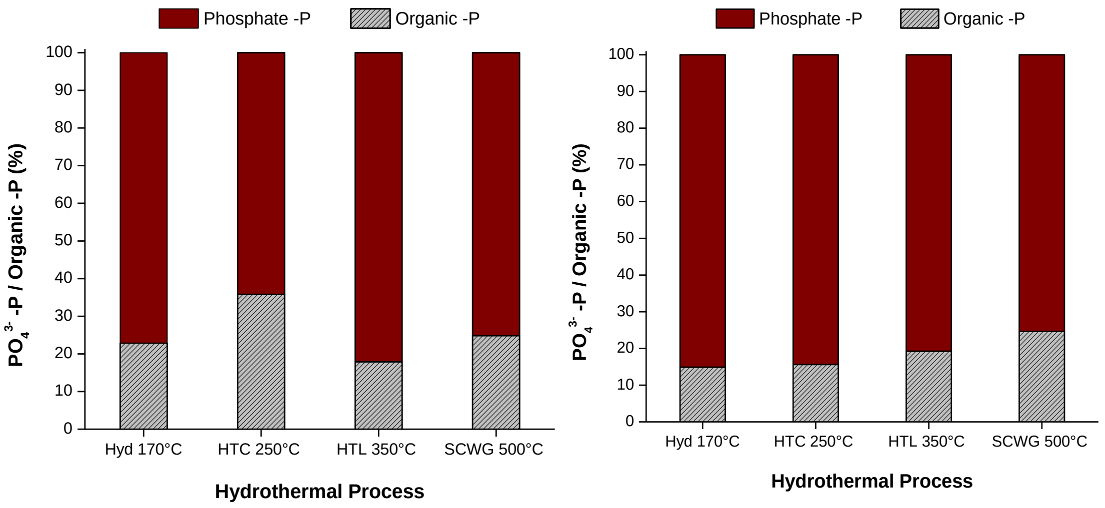
4.3.3.6 Forms of phosphorus present in the aqueous product

Figure 4-5 show the distribution of organic-P and phosphate-P in each of the aqueous products. As the process temperature increases, the organic-P (a complex fraction of phospholipids, DNA and phosphate monoesters) break down into phosphate-P (Dai et al., 2015). Following thermal hydrolysis of swine manure, organic-P accounts for about 12% of the total TP concentration while 88% was in the form of phosphate. As the conditions become more severe (350°C and 500°C), phosphorus in the aqueous products was mainly in the form of phosphate rather than organic-P.

This trend is similarly followed for chicken manure although for the digestate and microalgae, there are still considerable levels of organic-P present in the aqueous phase at the higher temperatures. For the microalgae, this may be due to the presence of phospholipids dissolved in the water. Previous studies on HTC of microalgae and distillers' grain have shown that phosphorus in the initial feedstock was mainly converted to soluble phosphate in the aqueous phase (Heilmann et al., 2011a;Heilmann et al., 2011b).

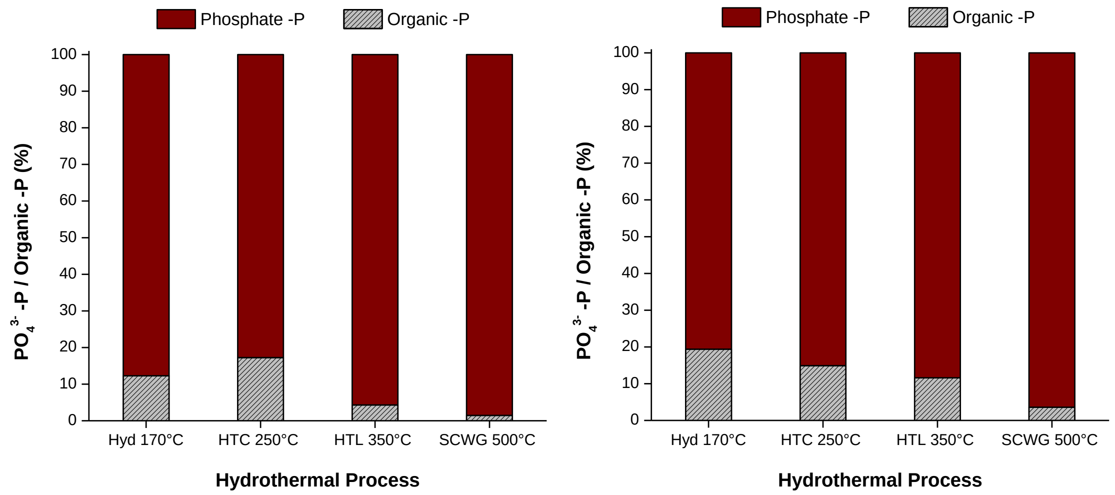
With manures however, the majority of phosphorus was retained in the hydrochar after HTC (Heilmann et al., 2014). It was concluded that the multivalent metal ions such as aluminium, calcium, magnesium and iron present in manures were most likely responsible for the formation of insoluble phosphate in colloidal forms or bound to proteins. This was confirmed with scanning electron microscopy and energy dispersive spectroscopy which indicated the presence of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$.

Calcium was found by Dai et al., (2015), to be higher in cow manure compared to Mg, Fe and Al and may be the main factor controlling the solubility of phosphorus in the solid residue. They concluded that the low solubility of phosphorus might be a result of apatite-P formed during HTC. In this study, swine and chicken manure had the highest level of Ca and Mg however the digestate contained significantly higher levels of iron and aluminium **Table 4-2**.



C.vulgaris

Digestate



Swine manure

Chicken manure

Figure 4-5: Forms of phosphorus present in the aqueous products from various feedstocks

Some of the feedstock exhibit immobilisation of the P whereas others behaved differently. For the swine manure and digestate, the levels of P are immobilised for each of the process conditions. *Chlorella* on the other hand releases phosphorus into the aqueous phase. The levels of P in the water are typically 40 wt. % after thermal hydrolysis and hydrothermal carbonisation, gradually reducing at the higher process severity. Chicken manure also releases significant levels of P after thermal hydrolysis but then reduces as the temperature increases beyond 250°C. The ratio of Ca: P in the microalgae is 0.74, i.e. there is more phosphorus than calcium, whereas for the swine manure, digestate and chicken manure, the Ca: P ratio is much higher at 2.36, 1.44 and 1.44 respectively. This may explain the increased extraction of P from microalgae but does not explain the extraction of P from chicken manure. The pH of the process waters following thermal hydrolysis are listed in **Table 4-7** and range from 4.9 to 5.1. The similar pH for process water suggests that the increased release of phosphorus from microalgae and chicken manure is not simply pH related.

Table 4-5 and **Table 4-6** list the metals in the residues following thermal processing and indicates a gradual increase in Ca and P content in the residue as the process severity increases. The microalgae residues once again contain a lower Ca: P ratio than the other feedstock however the Ca: P ratio for chicken manure is similar to swine manure. *Chlorella* and chicken manure produce slightly higher levels of organic P in the aqueous phase products possibly due to the presence of phospholipids or other organic P in the feedstock. After SCWG, the P is mainly associated with the solid product with low levels of extraction into the aqueous phase. Yildiz Bircan et al., (2011) reported that any feedstock containing N, P or S will decompose to NH_4^+, $PO_4^{\ 3-}$, $SO_3^{\ 2-}$ and SO_4^- during SCWG. After SCWG of O-phospho-DL-serine at 400°C, P was precipitated in the solid products. This was also observed for chicken manure in the presence of $Ca\ (OH)_2$ (Yildiz Bircan et al., 2011). All the feedstock investigated in this study immobilise phosphorus in the residue after SCWG. They contain the highest levels of Ca and other divalent metals and the pH ranges from 8.2 to 8.8 promoting precipitation.

4.3.3.7 Distribution of potassium

The results in **Figure 4-6** indicate that potassium is almost completely extracted under all conditions. Although potassium readily dissolves in water, there was an exception with digestate which shows only 56 wt. % recovery in the aqueous phase at 170°C. In the study by Sun et al. (2013), potassium was significantly affected with an increase in process temperature from 180 to 240°C and the concentration of dissolved potassium far exceeded the dissolved phosphorus. Potassium solubilisation increased from 50% to 70% when the temperature was increased from 180 to 240°C respectively.

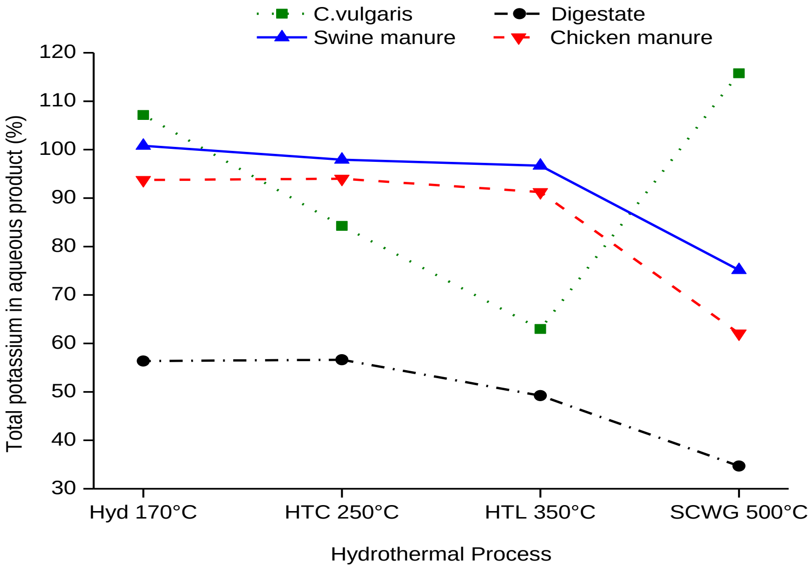


Figure 4-6: Extraction of total potassium into the aqueous phase

4.4 Conclusions

The results show that feedstocks behave differently during low temperature and high temperature hydrothermal processing with the composition and yields of by-product depending largely on the feedstock composition and processing temperature. The highest solid yields are obtained at the lowest temperature. About 45-60% solid yields from most feedstocks and 80% from digestate. Breakdown of organics occur with increasing temperature, forming gas and biocrude. Biocrude are formed during HTC but mostly during HTL (15-23% for most feedstocks) with little during SCWG and none during TH. However increased temperature during SCWG produces the most gaseous products (30-33% for most feedstocks and 55% for microalgae). Aqueous products contain significant quantities of essential plant nutrients- N,P,K. Aqueous products from lower temperatures contain higher phosphorus levels (mainly organic-P and less phosphate) and lower nitrogen levels (mainly organic-N and less NH_3-N) while it is vice versa at high processing temperatures. Microalgae and chicken manure released P more easily (40-43%) than swine manure and digestate (9-14%) at the lowest temperature- thermal hydrolysis. Although the levels of extracted P depends on the presence of inorganics such as Ca, Mg and Fe in the feedstock processed. At higher temperatures, P is immobilised in solid product and precipitated as phosphate salts. Higher TOC are present in aqueous products from lower temperatures and decrease with increasing temperature. Therefore aqueous products from either TH, HTC or HTL could be used as feedstock into the SCWG process for syngas production.

Chapter 5 Influence of pH on hydrothermal treatment of swine manure: Impact on extraction of nitrogen and phosphorus

5.1 Introduction

Although in the previous chapter (**Chapter 4**), four feedstocks – *C.vulgaris*, digestate, swine and chicken manure were used in the comparative study of four hydrothermal processing routes to determine the behaviour of these feedstock with increasing processing temperatures from 170°C to 500°C as well as the fate of nutrients during these processes. The results show that higher phosphorus extraction into the aqueous product occurred at lower temperatures with significant nitrogen as well. Whereas at higher temperatures, highest nitrogen was extracted into the aqueous products while phosphorus is mainly associated with the solid product. For this reason, to enhance nutrient extraction using additives, low-temperature hydrothermal processing (120°C - 250°C) was investigated in this study.

In this study, swine manure was selected as the sole feedstock to investigate the effect of changing pH of the reaction medium and its effect on nutrient extraction during low processing temperatures. Swine manure was chosen in part because it is easily obtained in sufficient quantity from the farm and also because it has similar composition with other livestock manures such as cattle manure and cow dung. Therefore the results obtained in this study will be beneficial for proper management of these kinds of manures.

This study aim is to enhance nutrient extraction from swine manure using various additives as solvent for the hydrothermal process. The study was based on two hydrothermal processes, Thermal hydrolysis and hydrothermal carbonisation. As illustrated in **Figure 5-1**, hydrolysis was used as a pre-treatment and was conducted at 120°C and 170°C while hydrothermal carbonisation was conducted at 200°C and 250°C. In each batch of experiment, 24g of biomass was made into a slurry using 220 mL of water or additive as the case may be and the residence time was 60 minutes. The various additives used in this study include alkali – 0.1M sodium hydroxide, mineral acid- 0.1M sulphuric acid and the organic acids, 0.1M acetic acid and 0.1M formic acid. The composition of the solid products and the aqueous products were determined using the various analytical methods mentioned in **Chapter 3**.

The effect of additives on nutrient extraction in this case nitrogen and phosphorus in the aqueous product were investigated.

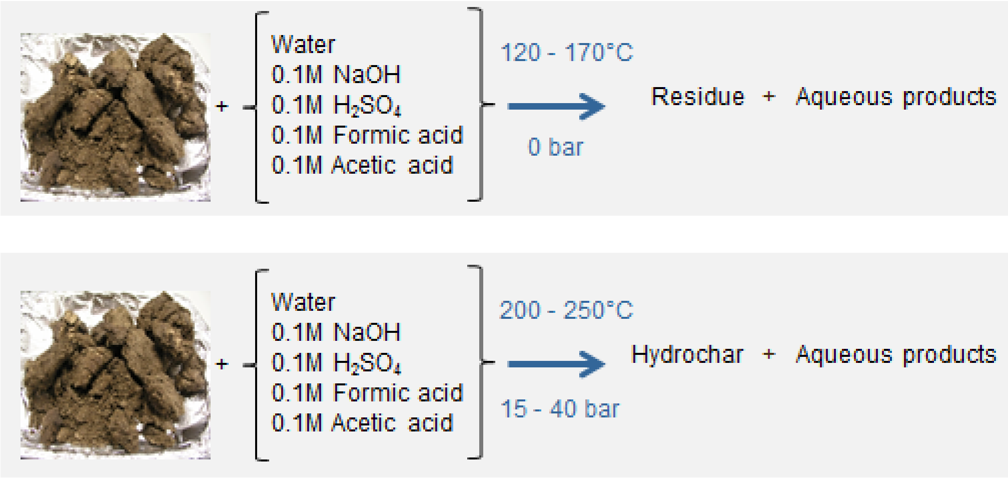


Figure 5-1: Overview of experimental work

5.2 Characterisation of the swine manure feedstock

5.2.1 Proximate and Ultimate analyses of swine manure

The proximate and ultimate analysis of the swine manure is listed in **Table 5-1**. The manure has a relatively high ash content (12.7 wt %). It was found to be about 18.1 wt% in the study by Tsai et al., (2012). The level of phosphorus in the manure is approximately 1.6 wt % which is about the same amount (1.7%) in the swine manure used in the study by Heilmann et al., (2014). Although poultry manure had slightly higher phosphorus (1.86 %) while the least phosphorus was present in cow manure (0.71%). The calorific value of the manure is 19.2 MJ kg^{-1} which is similar to 19.3 MJ kg^{-1} obtained in manure used by Tsai et al., (2012) and is towards the higher end compared to other biomass fuel (15 - 20 MJ kg^{-1}). It also contains about 22% fixed carbon and about 61% volatile matter. The percentage of combustible material is similar to the swine manure biomass used in the study by Tsai et al., (2012) in which it was about 68.3 wt%. Organic matter in swine manure could also be as high as 84 wt %, with about 25% crude protein and 22% crude lipids (Vardon et al., 2011). Swine manure is known to contain high levels of protein and lipids, which explains the high levels of Nitrogen (N) and Phosphorus (P) and the relatively high gross calorific value. Nitrogen content is about 5.03% in poultry manure, 4.88% in swine manure and 3.94% in cow manure on dry basis (Heilmann et al., 2014). Although in the nitrogen content of the manure used in this study was slightly lower (3.0 wt %). It has high carbon content of about 46.4% and oxygen content of about 31.4%. However similar values 42.2% and 36.4% were obtained respectively for swine manure in the study by (Tsai et al., 2012).

Table 5-1: Composition of dried swine manure

Biomass	**Proximate analyses (%)**				**Ultimate analyses [a] (%)**						Conc. (mg kg^{-1})
	Moisture	Ash [a]	Volatiles	Fixed carbon	C	H	N	S	O[b]	HHV (MJ Kg^{-1})	Phosphorus
Swine manure	5.3	12.7	61.1	21.6	46.4	6.3	3.0	0.2	31.4	19.2	15,580

[a] dry basis

[b] calculated as difference between sum of C, H, N, S, Ash

5.3 Influence of additives on the aqueous products

The processing of the manure in different reagents allows the influence of pH on N and P extraction to be investigated.

5.3.1 Effect on the pH and TOC of the aqueous products

The use of the acidic reagents (e.g., formic acid, acetic acid and sulphuric acid) resulted in a range in pH between 1.0 and 2.8. The use of the basic reagent sodium hydroxide had a pH of 12.8. The baseline condition using de-ionised water was neutral at pH 7.

The pH of the aqueous products was measured after the hydrothermal process and the results are shown in **Table 5-2**. The processing of the manure in water at each temperature consistently results in a reduction in the pH after extraction. This reduction increases as the temperature increases from 120^{o}C to 250^{o}C. This reduction in pH is due to the formation of organic acids which dissolve in the process water and is typical of hydrothermal carbonisation in water alone. The aqueous product from HTC contain acetic acid, other organic acids as well as sugars (Hoekman et al., 2011; Lynam et al., 2011). When the manure is processed in the presence of NaOH, the pH similarly reduces as the temperature increases. At 120^{o}C the pH is still basic and has reduced from 12.8 to 8.2 but as the temperature increases, the pH gradually reduces and ranges between 5.5 and 6.0 after 200^{o}C. The processing of the manure using the acidic reagents results in the opposite effect, the pH is increased for all reagents although there is little difference between each temperature. The initial pH of the H_2SO_4 at <1.0 results in a final pH between 3.5 and 3.8. The initial pH of the formic acid and acetic acid were between 2.0 and 3.0 respectively which increased to typically 4.2 to 4.9. This increase in pH is likely due to the increase in ammonium in solution and other basic nitrogen compounds present in the water. Previous studies have shown that under hydrothermal conditions, both acetic and formic acids are consumed with a reduction in acetate and formate levels (Ross et al., 2010). This was also observed by Lynam et al. (2011) during HTC, who also suggested that it was indicative of the shift in concentration between the quantities of reactants and products which are in equilibrium.

TOC in the aqueous products is indicative of the proportion of organic products which are water soluble. Generally, the TOC in the process waters remains relatively constant at each temperature irrespective of the reagents used. The nature of the organic material generally includes organic acids, sugars and fatty acids although the exact nature of this organic material is beyond the scope of this study.

Table 5-2: pH, total organic carbon (TOC), nitrogen and phosphorus in the aqueous products

Hydrothermal Process	pH	Concentration (mg/L)				
		TOC	NH_3-N	TKN	PO_4^{3-}	TP
Hyd 120°C						
water	6.2	8904	409	1228	560	652
0.1M NaOH	8.2	13272	294	1544	203	287
0.1M H_2SO_4	3.7	10410	428	1239	1687	1801
0.1M Formic acid	4.5	9195	377	1031	384	507
0.1M Acetic acid	4.8	10365	361	1028	404	550
Hyd 170°C						
water	5.1	17760	624	1767	216	244
0.1M NaOH	7.3	18521	723	1915	266	319
0.1M H_2SO_4	3.5	17814	851	2144	2022	2200
0.1M Formic acid	4.2	16746	496	1617	373	390
0.1M Acetic acid	4.5	18678	485	1615	391	400
HTC 200°C						
water	4.6	14520	434	1682	103	106
0.1M NaOH	5.5	16815	392	1805	76	86
0.1M H_2SO_4	3.6	12848	756	1832	1468	1494
0.1M Formic acid	4.2	15111	572	1752	209	211
0.1M Acetic acid	4.3	16973	499	1747	168	168
HTC 250°C						
water	4.7	14261	534	1469	13	14
0.1M NaOH	6.0	16231	570	1451	12	13
0.1M H_2SO_4	3.8	12093	706	1659	1050	1052
0.1M Formic acid	4.9	14679	537	1545	15	15
0.1M Acetic acid	4.5	16875	538	1512	38	44

5.3.2 Fate of nitrogen following hydrothermal treatment at different pH.

Table 5-2 shows the concentrations of ammonium and total nitrogen present in the aqueous products after thermal hydrolysis at 120°C and 170°C as well as during hydrothermal carbonisation at 200°C and 250°C respectively. Generally the ammoniacal nitrogen (NH_3-N) increases with process temperature raising from 120°C to 250°C. As stated by Sun et al. (2013), reaction temperature plays a significant role in nitrogen solubilisation. Similarly in the study by Ekpo et al. (2016), NH_3-N significantly increased as the process severity increased from 170°C to 500°C. The levels of extracted NH_3-N are affected by pH and is generally highest using H_2SO_4 and lowest using NaOH. The levels of NH_3-N for H_2SO_4 range from 430 mg/L at 120^oC up to a maximum of 850 mg/L at 170^oC. The effect of temperature on the levels of NH_3-N in water, NaOH and organic acids were significantly less than with H_2SO_4.

Generally, the highest levels of TN-N are extracted between 170 and 200^oC. For processing with H_2SO_4 the peak TN-N concentrations is at 170^oC and reaches over 2,000mg/L. The extraction of TN-N generally peaks at 170^oC and then reduces as the temperature increases.

Figure 5-2 show the distribution of organic-N and NH_3-N in the aqueous phase. The difference between the TN-N and NH_3-N is attributed to the organic-N fraction in the aqueous product. Each of the aqueous products contain high levels of organic-N for all hydrothermal conditions. The levels of organic-N and NH_3-N are shown in **Table 5-2**. Extraction of organic-N once again peaks between 170^oC and 200^oC and then reduces. The highest organic-N is observed at 200^oC in water and NaOH and the highest level of NH_3-N is observed at 170^oC using H_2SO_4. The organic-N typically represents between 60-70 % of the N in the aqueous product. Even at 250^oC, the organic-N is still 60% of the total-N. In comparison, Ekpo et al., indicated that higher temperature hydrothermal processing (HTL and SCWG) degraded organic-N significantly increasing the levels of NH_3-N (Ekpo et al., 2015).

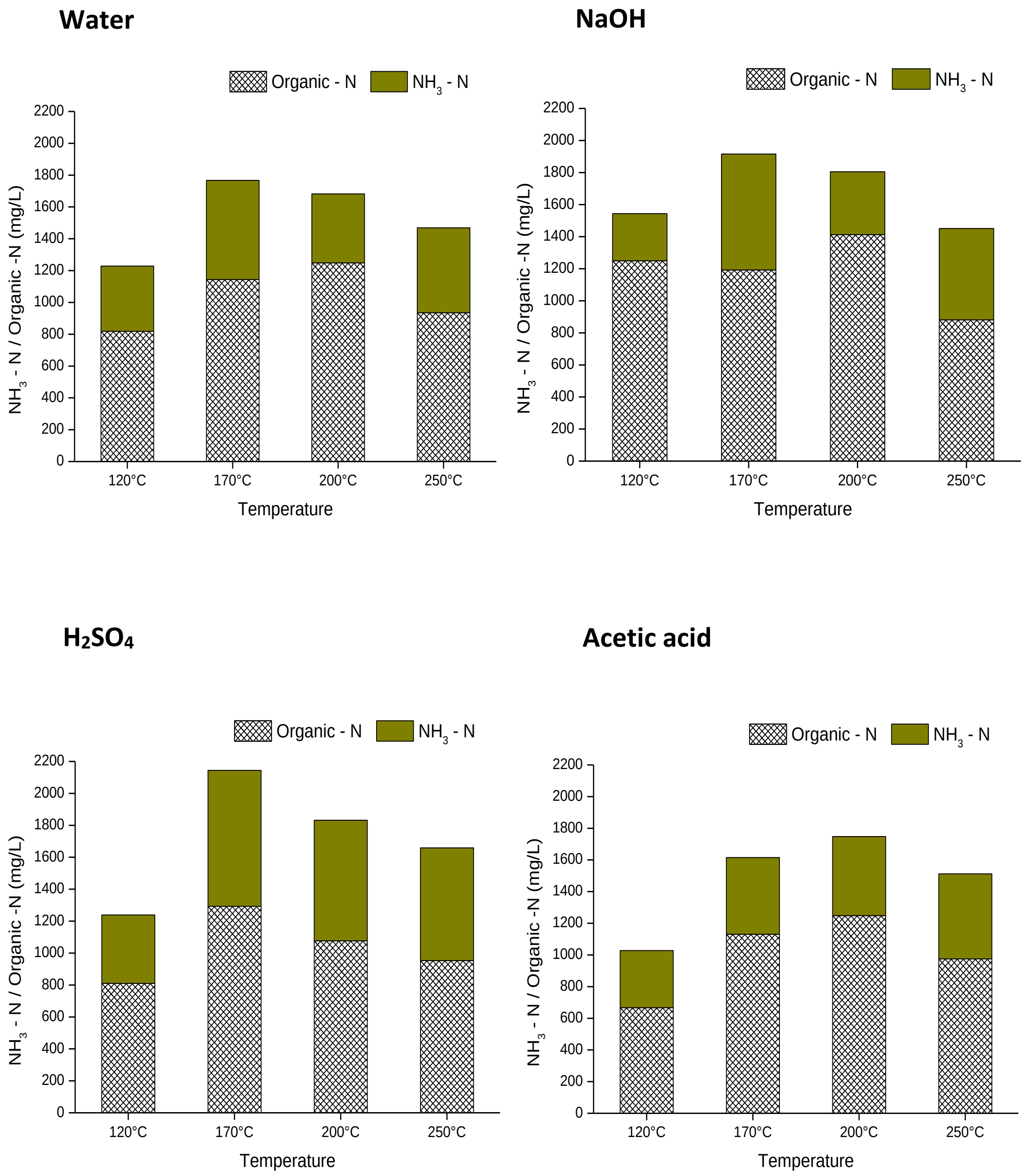
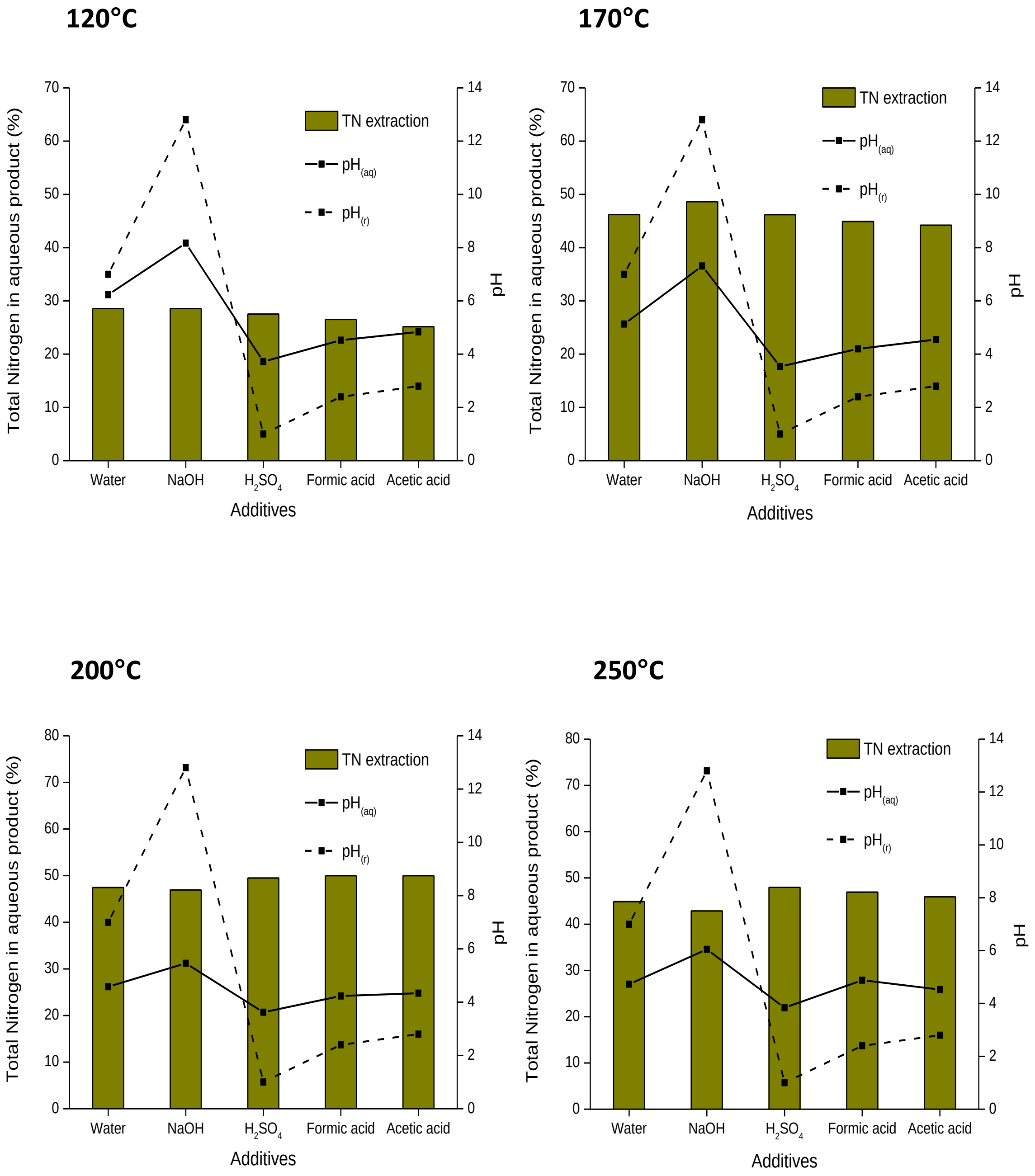


Figure 5-2: Forms of nitrogen present in the aqueous products using various additives

Figure 5-3 shows the % extraction of total nitrogen from the raw feedstock into the aqueous product for each of the different reagents. The % of N extraction increases up to 170°C and then remains relatively constant. The extraction of nitrogen was not significantly affected by pH at any given temperature. During thermal hydrolysis at 120°C, nitrogen extraction was between 25 - 29% for all additives. Although nitrogen extraction during thermal hydrolysis at 170°C was almost double compared with the extraction observed at 120°C, similar extraction levels were observed for all additives at this temperature ranging from 44 to 49%. During HTC 200°C, extraction was between 47 - 50% while during HTC 250°C, it was between 43 - 48%.



*pH(r) – pH of the starting reagent, *pH(aq) – pH of the recovered aqueous products

Figure 5-3: Nitrogen extraction during thermal hydrolysis and HTC

5.3.3 Fate of phosphorus following hydrothermal treatment at different pH.

Table 5-2 shows the concentrations of reactive and total phosphorus present in the aqueous products after thermal hydrolysis at 120°C and 170°C as well as during hydrothermal carbonisation at 200°C and 250°C respectively.

For each experiment, the level of reactive phosphorus was measured and compared to the total phosphorus. **Figure 5-4** show the forms of phosphorus present in the aqueous products. The organic-P fraction in the aqueous product was determined by difference between total and reactive phosphorus. Significant quantities of organic-P were observed in the aqueous products from thermal hydrolysis and HTC. This observation was similar to the study by Ekpo et al. (2016) in comparison with high-temperature hydrothermal processing (i.e., Hydrothermal Liquefaction - HTL and Supercritical Water Gasification - SCWG), which had much lesser organic-P.

Following thermal hydrolysis at 120°C, the highest concentration of phosphorus (1,800 mg/L) was observed in the pre-treatment with H_2SO_4 while the lowest concentration of phosphorus (290 mg/L) was observed in the pre-treatment with NaOH. The concentration of total phosphorus during the pre-treatment with the organic acids-formic and acetic, was observed to be 510 mg/L and 550 mg/L respectively while it was 650 mg/L with de-ionised water. The distribution of phosphorus in the recovered aqueous phase from the hydrolysis pre-treatment at 120°C indicated that organic phosphorus accounts for 29% of the total phosphorus using NaOH, between 24 - 27% using formic and acetic acid respectively while it was about 14% using de-ionised water. The least organic phosphorus (about 6%) was observed in the aqueous product using H_2SO_4.

Following hydrolysis at 170°C, a higher phosphorus concentration (2,200 mg/L) was observed in the aqueous phase with H_2SO_4. A similar phosphorus concentration was observed using both organic acids; 390 mg/L from formic acid and 400 mg/L from acetic acid, while it was slightly lower using NaOH (320 mg/L) and de-ionised water (240 mg/L). At 170°C, the organic phosphorus decreased by 3%, 12%, 20% and 24% when using de-ionised water, NaOH, formic acid and acetic acid respectively. The organic fraction using H_2SO_4 at 120°C and 170°C was fairly constant ranging between 6 - 8%.

The phosphorus concentration observed during hydrothermal carbonisation was much lower than the quantities extracted during thermal hydrolysis. Although at HTC 200°C, H_2SO_4 extracted the most phosphorus (1,490 mg/L) which was seven-fold higher than the amount extracted with formic acid (210 mg/L). Among the organic acids used, formic acid extracted more phosphorus into solution than the acetic acid, which was about 170 mg/L. Extraction of phosphorus using de-ionised water and NaOH were even lower with about 110 mg/L and 90 mg/L respectively. At this temperature, it was observed that most of the phosphorus present in solution was readily available in the form of phosphate with the organic fraction representing between 0 - 3% when the mineral acid, organic acid and de-ionised water was used. A significant quantity of organic phosphorus (12%) remained in the aqueous phase when NaOH was used as reagent.

At 250°C, de-ionised water, NaOH and formic acid extracted similar concentrations of phosphorus at 10 mg/L, 10 mg/L and 20 mg/L respectively. However among the organic acids, using acetic acid extracted more phosphorus (40 mg/L). In comparison with all other additives used at this temperature, H_2SO_4 extracted the most phosphorus at about 1050 mg/L. There was no organic phosphorus left in the aqueous product from de-ionised water, H_2SO_4 and formic acid. Small quantities of organic phosphorus (8 - 14%) were observed in the aqueous product from NaOH and acetic acid.

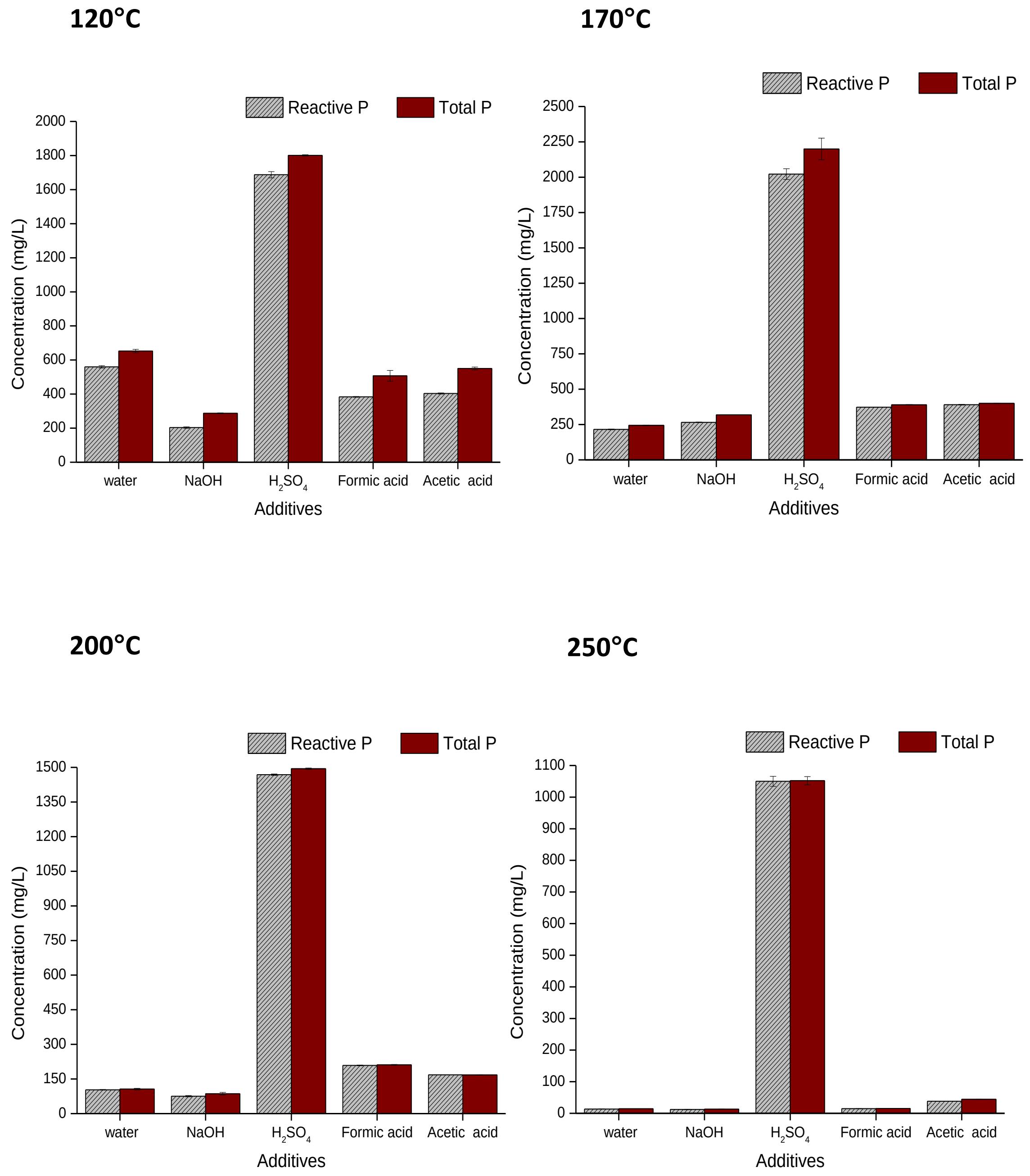
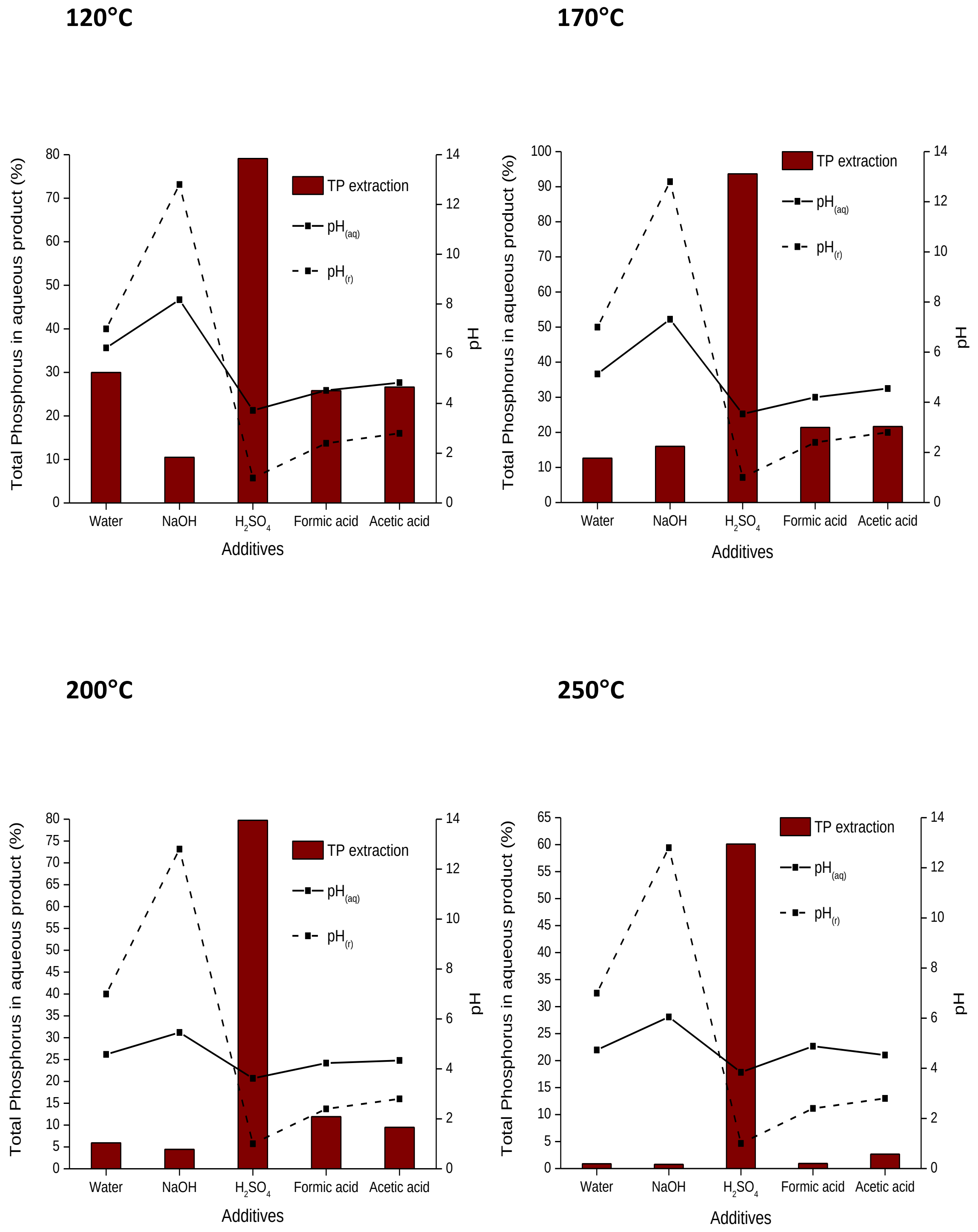


Figure 5-4: Forms of phosphorus present in the aqueous products after thermal hydrolysis and HTC

Higher dissolution of Ca, Mg, Al phosphates to inorganic-P occur with acid treatments, releasing organic-P which are products of phytate hydrolysis and hydrolysis of monoester-P compounds (Pagliari and Laboski, 2012). The difference between the soluble total phosphorus (TP) and the reactive phosphorus (RP) is the soluble unreactive phosphorus which is mainly organic forms of phosphorus containing condensed polyphosphates (Szogi et al., 2015). The reactive phosphorus represents inorganic phosphorus and loosely-bound organic forms of phosphorus released during hydrolysis (Szogi et al., 2015). There was effective solubilisation of inorganic-P compounds by the mineral acid and organic acid additives and therefore, that represented a huge fraction of the recoverable phosphorus from this feedstock.

Figure 5-5 show the relationship between pH of the starting reagent and its effect on the extraction of total phosphorus from the raw feedstock into solution. Generally, the results show higher extraction of phosphorus is achieved under acidic conditions. The addition of the different reagents affects the pH of the recovered aqueous product. Typically using water and NaOH, the pH of the aqueous product reduces whereas with the acidic reagents, the pH of the aqueous products increases.

Following thermal hydrolysis at 120°C in water alone, 30% of the phosphorus present in the feedstock was extracted into solution. Thermal hydrolysis in alkali- NaOH results in the lower extraction of 11%. The use of organic acids behaves similarly to water alone and extract between 26 - 27% of the total phosphorus. The highest extraction of phosphorus is achieved using H_2SO_4 and represents 79% of the total.



*pH(r) – pH of the starting reagent, *pH(aq) – pH of the recovered aqueous products

Figure 5-5: Phosphorus extraction during thermal hydrolysis and HTC

Following thermal hydrolysis at 170°C, the extraction of phosphorus in water alone reduces to 13% while extraction of phosphorus using formic acid and acetic acid also reduces to 21% and 22% respectively. Extraction in NaOH extracts 16% of the total phosphorus, a slight increase compared to extraction at 120^{o}C. Once again the extraction of phosphorus was highest with H_2SO_4 reaching the maximum extraction of 94% of the total.

Extraction of phosphorus following hydrothermal carbonisation was generally lower compared to thermal hydrolysis. At 200°C, only 6% of the phosphorus was extracted in water alone. The extraction in alkali reduced four-fold compared to following thermal hydrolysis at 170°C. Extraction in organic acids also decreased by 9% and 13% when compared to thermal hydrolysis at 170°C. While the extraction in H_2SO_4 was the highest, it is starting to decrease and represents 80% of the total. But this has reduced compared to thermal hydrolysis at 170^{o}C. At 250°C, very little phosphorus is extracted in water alone, alkali or organic acids (1-3%). The extraction in H_2SO_4 reduces to 60% indicating that the higher the temperature, the more the phosphorus is associated with the solid residue (Ekpo et al., 2016).

The extraction of phosphorus in water alone increases as the temperature reduces in agreement with the results described by Szogi et al., who reported that 49% of the total phosphorus can be extracted from manure at ambient temperatures in water alone (Szogi et al., 2014). The 'quick wash' process described by Szogi et al., is operated at ambient temperature and extracts phosphorus from raw manure followed by recovery into a concentrated solid form (calcium phosphate) by the addition of lime and an organic polymer (Szogi et al., 2014). The extraction of phosphorus is increased by adding mineral and organic acids and the type of acid was shown to influence phosphorus extraction. At equal molar concentrations, citric acid was shown to be more effective at extracting phosphorus than HCl, achieving 87% and 75% respectively. The use of HCl for phosphorus extraction is not ideal due to the presence of chloride in the aqueous product. The extraction of phosphorus at 170^{o}C in H_2SO_4 reaches 94% of the total and is therefore higher than the 'quick wash' approach, however the use of H_2SO_4 could be more corrosive and promote oxidation of organic material.

5.4 Mass balance of nitrogen and phosphorus following hydrothermal treatment

The results show that during thermal hydrolysis of swine manure at 120°C, about 61-65% of the total nitrogen present in the unprocessed feedstock remained in the hydrochar from de-ionised water and NaOH while the hydrochar from H_2SO_4, formic acid and acetic acid contained between 71 - 74% of the total nitrogen in the unprocessed feedstock. At this temperature, more phosphorus remained in the hydrochar (63 - 84%) than the aqueous phase for all additives (11 - 30%) except the H_2SO_4. In particular, with H_2SO_4, about 79% of the phosphorus was extracted into the aqueous product leaving about 11% in the hydrochar. At 170°C, nitrogen was almost equally distributed between the hydrochar and the aqueous phase for all additives as well as de-ionised water. Higher extraction of phosphorus (94%) occurred again with H_2SO_4, with less than 6% in the hydrochar. Most of the phosphorus (between 77 - 92%) remained in the hydrochar from de-ionised water, NaOH and organic acids.

During HTC 200°C, nitrogen was almost equally distributed between the hydrochar and the aqueous phase for all additives as well as de-ionised water. About 98% of the total phosphorus present remains in the hydrochar using water and NaOH, 86 - 87% using organic acids and 17% using H_2SO_4. This implies that extraction of phosphorus was highest (80%) with H_2SO_4, although the amount extracted was lower compared to thermal hydrolysis. During HTC 250°C, nitrogen distribution between the hydrochar and the aqueous phase was almost similar with HTC 200°C while 91 - 97% of the total phosphorus present remained in the hydrochar using de-ionised water and NaOH, more than 98% using organic acids and only 36% using H_2SO_4.

5.5 Conclusion

The aqueous product from both thermal hydrolysis and HTC contain significant amounts of nutrients- N and P. Under neutral or alkali conditions, the recovered aqueous pH is acidic. Reduction in pH is increased with increasing temperature. Under acidic conditions, the recovered aqueous pH is increased. Aqueous products from thermal hydrolysis and HTC contain significant levels of organic-N and organic-P. Nitrogen extraction is significantly affected by temperature rather than pH. NH_3-N extracted increases with increasing temperature and is affected by pH, highest levels achieved with mineral acid and lowest level with alkali. Highest TN are extracted between 170-200°C and remains constant afterwards. TN extraction not affected by pH. High organic-N (60-70%) in all aqueous products. Organic-N is highest between 170-200°C and then reduces with increasing temperature. Organic-P fraction reduces under acidic conditions especially with H_2SO_4. Generally phosphorus extraction is pH and temperature dependent. Extraction of phosphorus reduces with increasing process temperature. Acidic conditions favour higher phosphorus extraction particularly with the addition of a mineral acid (H_2SO_4) at all temperatures and presents an opportunity for nutrient recovery. At higher temperatures, phosphorus is readily available as inorganic-P (phosphate) with less than 3% organic-P for most additives but significant quantities of organic-P present using NaOH.

At 120°C, N is mainly present in solid products; 61-65% using water and alkali and 71-74% under acidic conditions. About 63-84% P is present in the solid products, extracting 11-30% into solution using most additives however with H_2SO_4, 11% P is in solid with about 79% extraction. At 170°C, equal distribution of N in both aqueous and solid, 77-92% P in solid for most additives; only 6% P with H_2SO_4 resulting in highest extraction (94%). At HTC 200°C, equal distribution of N, concentration of P in solid; 98% using water and NaOH, 86-87% with organic acid and 17% with H_2SO_4 resulting in 80% extraction. At HTC 250°C, equal distribution of N, P concentrated more in solid; 91-98% for most additives and 36% using H_2SO_4.

Chapter 6 Influence of pH on hydrothermal treatment of swine manure: Impact on metals

6.1 Introduction

In **Chapter 5**, the effect of using various additives as solvent for low-temperature hydrothermal processing of swine manure was investigated with the focus mainly on the fate of nutrients. Thermal hydrolysis was performed at 120°C and 170°C while hydrothermal carbonisation was performed at 200°C and 250°C. However in this chapter, the focus is mainly on the fate of metals during these two processes. The effect of additives on metal extraction and metal retention in the aqueous and solid products was investigated. The process conditions and experimental setup stated in **Chapter 5** is the same in this chapter.

6.2 Composition of inorganics

Table 6-1 lists the metal content present in the swine manure feedstock in mg kg^{-1}. The composition of these metals in wt.% has been presented in **Figure 6-1**. Calcium was highest (31,690 mg kg^{-1}) among all the other elements, and accounts for about 3.2 wt.%. Straws are usually used as bedding materials in swine units and are high in calcium. During animal manure collection, some of the straw material are collected along with the manure. As shown in **Table 5-1**, phosphorus is the second major nutrient (15,580 mg kg^{-1} and accounts for 1.6 wt. % which implies that the Ca: P ratio is 2. The concentration of potassium and magnesium is about 1.2 wt. % and 0.9 wt. % respectively, however sodium is the least (0.3 wt. %) macronutrient present in the feedstock. Micronutrients are also present in smaller quantities compared to macronutrients. Iron was the highest micronutrient (0.1 wt. %) followed by zinc (0.07 wt. %). Compared to the amount of zinc present, the quantity of manganese was almost half the concentration of zinc (0.04 wt. %) while copper was significantly lower (0.02 wt. %). Cobalt was hardly present in this feedstock. The heavy metals were less than 0.06 wt. %.

Table 6-1: Metals present in dried swine manure

	Concentration (mg kg^{-1})											
Biomass	K	Ca	Mg	Na	Fe	Al	Ni	Co	Cu	Pb	Mn	Zn
Swine manure	12,120	31,690	9,240	3,030	1,050	480	30	1	160	2	370	690

*Analysis by ICP-OES

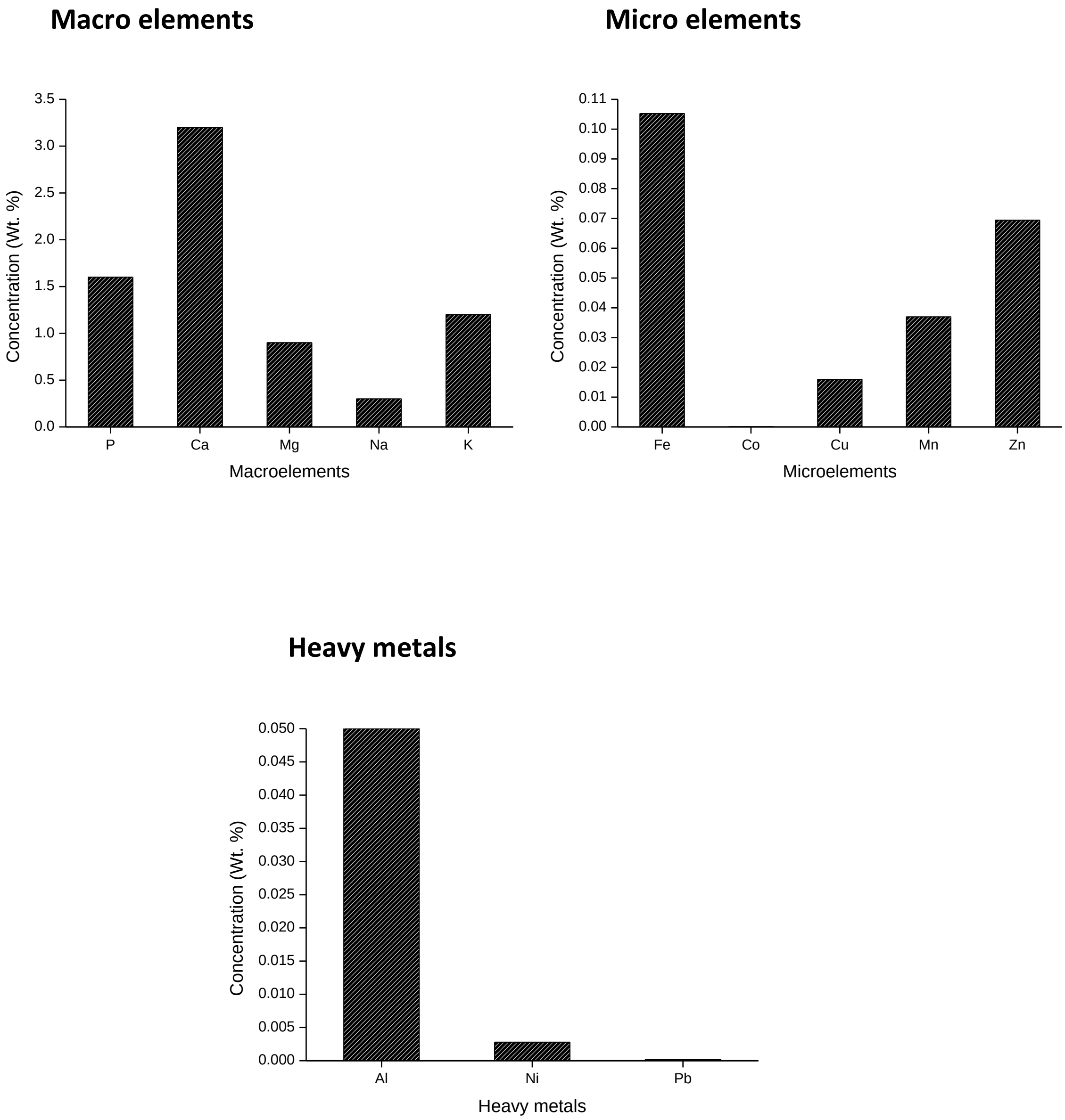


Figure 6-1: Inorganic composition of swine manure

6.3 Influence of additives on hydrochar products

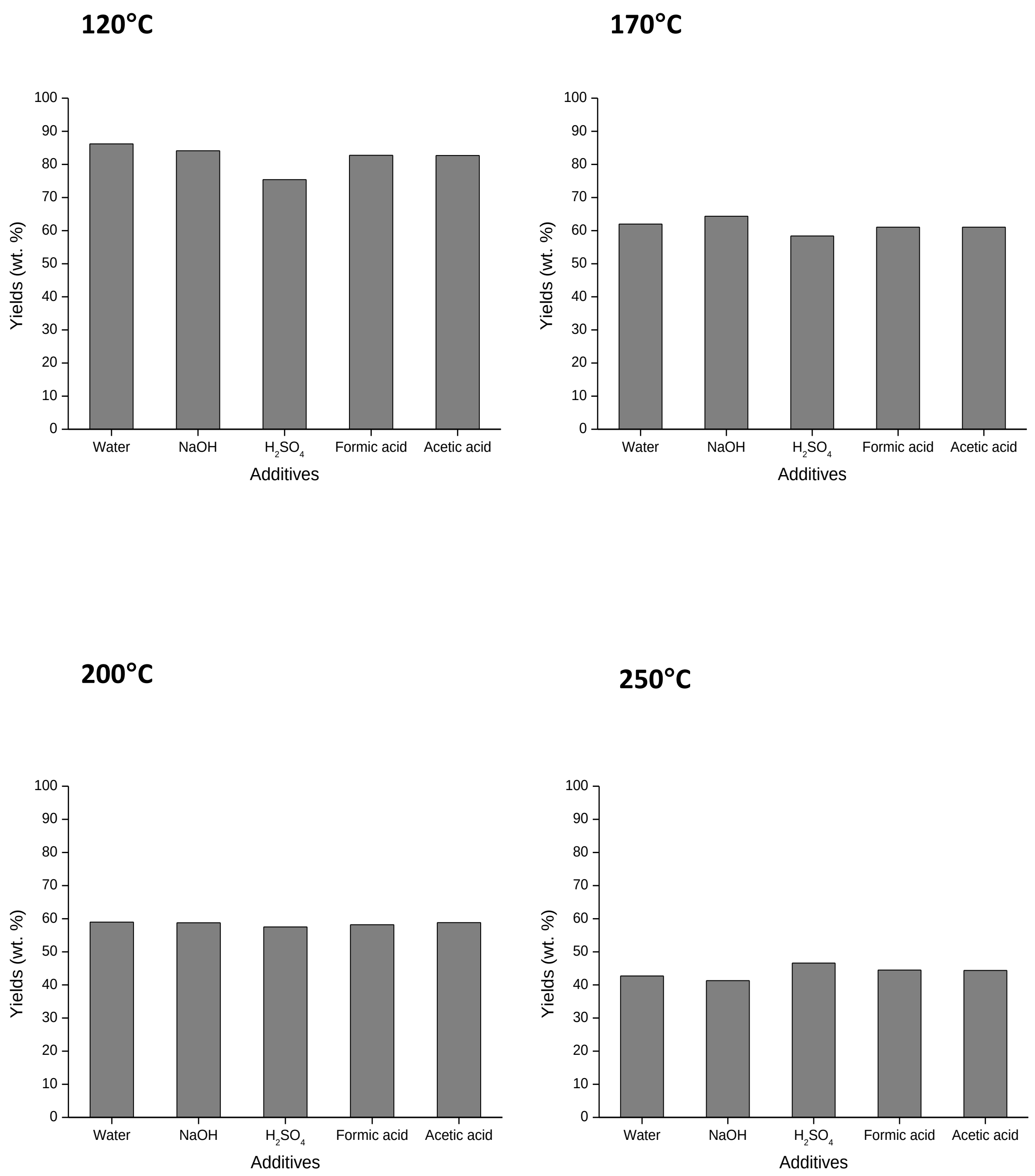
The effect of additives and processing temperature on solid yields, elemental composition, ash content, volatiles and phosphorus in the solid products were analysed. However the chemical and morphological properties of these hydrochar were not studied as it is beyond the scope of this study.

6.3.1 Effect of temperature and pH on solid yields

The yields of residue following hydrothermal treatment as shown in **Figure 6-2** reduce as the temperature of processing increases. The decrease in solid product is accompanied by an increase in soluble organic material in the aqueous product.

The typical solid yield from hydrolysis at 120°C was in the range of 83 - 86% for all additives investigated except for H_2SO_4 which gave a lower yield of about 75%. During thermal hydrolysis at 170°C, the solid product yield reduces to between 61 - 64% for all additives investigated, however the solid yield from H_2SO_4 was once again slightly lower at 58%.

Similar solid yields were obtained during HTC 200°C, 59% was obtained with de-ionised water (pH 7), NaOH (pH 12.8) and acetic acid (pH 2.8) while 57% and 58% was obtained using H_2SO_4 (pH <2) and formic acid (pH 2.4) respectively. HTC 250°C with H_2SO_4 gave a higher solid yield (47%) while the yields for the other additives at this temperature was between 41- 44%. Comparing the change in solid yield with an increase in temperature and the change in solid yields using the various additives, it is obvious that process temperature greatly affects the solid yields rather than pH. This trend was observed by Reza et al., (2015), although their study focused mainly on HTC rather than thermal hydrolysis. In the study by Lu et al., (2014), they performed HTC of cellulose with different types of feedwater such as mineral acids- HCl and H_2SO_4, organic acid- acetic acid and alkali- NaOH and $Ca(OH)_2$. It was concluded that these additives had no significant effect on solid yields.



120°C

170°C

200°C

250°C

Figure 6-2: Solid yield using additives during thermal hydrolysis and HTC

6.3.2 Effect on elemental composition and energy content of hydrochar

Table 6-2 shows the results from proximate and ultimate analyses for all the recovered solid products. Also the composition of phosphorus retained in the hydrochars is presented as well.

Table 6-2: Elemental composition of solid products

	Proximate analyses (%)				**Ultimate analyses [a] (%)**						Wt. %
Biomass	Moisture	Ash [a]	Volatiles	Fixed carbon	C	H	N	S	O[b]	HHV (MJ Kg^{-1})	P
120°C											
water	5.8	13.8	66.9	14.3	46.0	6.4	2.3	0.1	31.3	19.2	1.1
NaOH	5.8	14.4	65.1	15.6	45.5	6.3	2.2	0.0	31.6	18.7	1.5
H_2SO_4	4.5	9.0	72.3	14.6	49.8	6.6	2.8	0.4	31.3	20.8	0.2
Formic	4.3	12.3	69.3	14.6	49.2	6.6	2.6	0.3	29.1	20.9	1.3
Acetic	5.0	11.3	70.2	14.1	48.6	6.4	2.7	0.2	30.9	20.1	1.2
170°C											
water	3.6	14.8	66.3	15.9	48.9	6.3	2.1	0.1	27.8	20.6	2.0
NaOH	4.4	17.0	65.2	14.2	47.8	6.5	2.0	0.0	26.6	20.8	2.2
H_2SO_4	2.7	11.4	71.2	15.0	52.9	6.4	2.6	0.6	26.2	22.4	0.2
Formic	2.9	14.2	66.4	16.9	52.0	6.5	2.7	0.2	24.3	22.6	1.9
Acetic	3.4	13.3	68.6	15.1	51.0	6.4	2.6	0.1	26.5	21.8	1.9
200°C											
water	2.9	14.9	66.1	16.5	51.4	6.0	2.3	0.1	25.2	21.6	2.5
NaOH	2.8	17.1	63.1	17.5	49.7	6.1	2.3	0.3	24.5	21.3	2.5
H_2SO_4	2.4	10.6	67.9	19.4	54.6	6.2	2.3	0.5	25.8	22.8	0.4
Formic	2.3	14.5	64.6	19.0	53.1	6.2	2.3	0.2	23.7	22.7	2.2
Acetic	2.6	15.5	64.1	18.3	53.3	6.3	2.4	0.1	22.5	23.1	2.2
250°C											
water	2.1	21.6	54.8	21.9	56.2	6.0	2.7	0.1	13.3	25.3	3.4
NaOH	1.9	27.0	50.5	21.1	50.7	5.5	2.5	0.2	14.0	22.6	3.2
H_2SO_4	1.4	15.8	57.0	26.0	63.0	6.1	3.1	1.9	10.0	28.5	1.1
Formic	1.6	19.1	56.9	22.7	57.9	6.2	2.9	0.2	13.7	26.0	3.3
Acetic	1.9	21.1	53.0	24.4	58.4	6.1	2.9	0.2	11.4	26.5	3.4

[a] dry basis

[b] calculated as difference between sum of C, H, N, S, and Ash

6.3.2.1 Effect of temperature and pH on total ash content

The effect of processing temperature on the total ash content in the solid products from the various additives and de-ionised water was investigated. The results are presented in **Table 6-2** and illustrations of the effect of temperature and additives on the total ash content are shown in **Figure 6-3.**

Generally for all additives and under normal conditions with de-ionised water, the total ash content of the solid increased with increase in process temperature. For instance, under normal conditions with de-ionised water, ash content increased slightly from 13.8 wt % at 120°C to 14.9 wt % at 200°C. As the temperature increased from 200°C to 250°C, there was a significant increase in ash which was about 6.7 wt %.

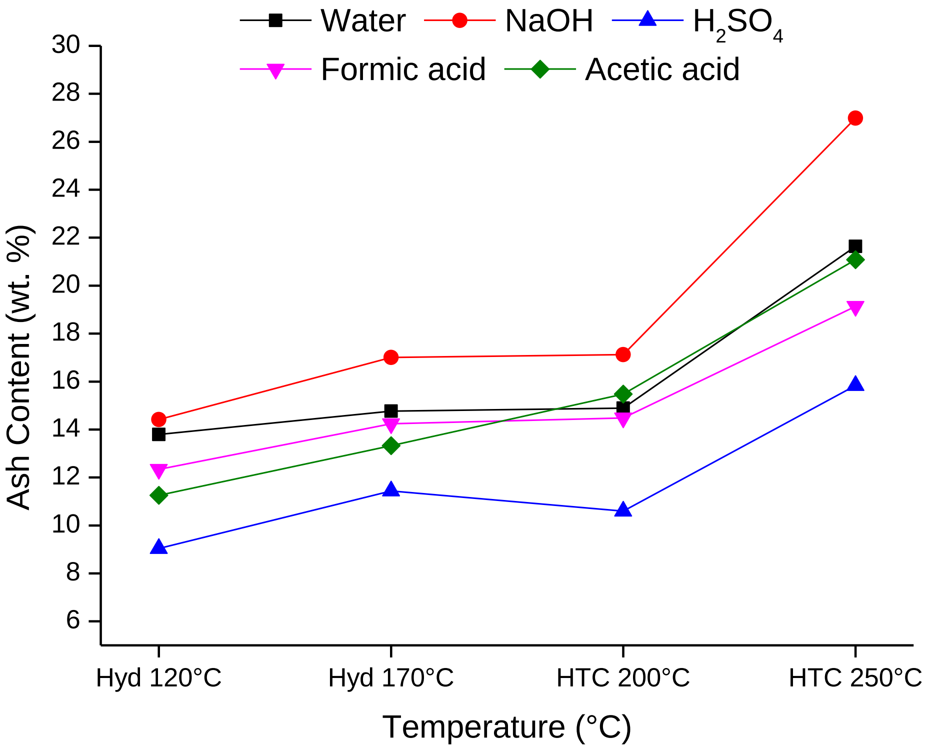


Figure 6-3: Effect of temperature and additives on total ash content

In addition to temperature, pH also has an effect on ash content. During hydrolysis and HTC, generally neutral and alkali conditions increased ash content in the solid products compared to acidic conditions. For instance at 250°C (most severe temperature investigated), the solid product recovered from alkali treatment had the highest ash content (27 wt %) while the least ash content (16 wt %) at this temperature was observed in the solid recovered from mineral acid treatment.

6.3.2.2 Volatile content

Table 6-2 also shows the trend with volatile content of the recovered solid products. Generally, volatile content decreases as temperature increases from 120 -250°C. However at a given temperature, the use of additives had little effect on the volatile content.

6.3.2.3 Energy content

The individual energy content of the hydrochars recovered are shown in **Table 6-2**. **Figure 6-4** compares the energy content of the residues and hydrochars with the energy content of the unprocessed swine manure feedstock. The energy content in the solid products increased with increase in temperature. Compared to the raw swine manure feedstock with energy content 19.2 MJ kg^{-1}, hydrothermal treatment increased the energy content in all the recovered solid products. The energy content of hydrochar strongly depends on its elemental carbon as a higher carbon in the hydrochar makes it more suitable for carbon sequestration, production of carbon based materials and as a soil amendment. Generally for the temperatures investigated, the hydrochars from acidic reagents had more energy content compared to hydrochars from neutral or alkali conditions. In particular, hydrochars from H_2SO_4 and formic acid had similar energy content at temperatures between 120-200°C. However at 250°C, the energy content in the H_2SO_4 hydrochar increased significantly to 28.5 MJ kg^{-1} from 22.8 MJ kg^{-1} at 200°C.

The results in **Chapter 5** show that higher phosphorus extraction levels are obtainable with mineral acid compared to other additives. However with mineral acid also, HHV of the hydrochar is increased significantly which increases its potential value as a suitable feedstock for combustion.

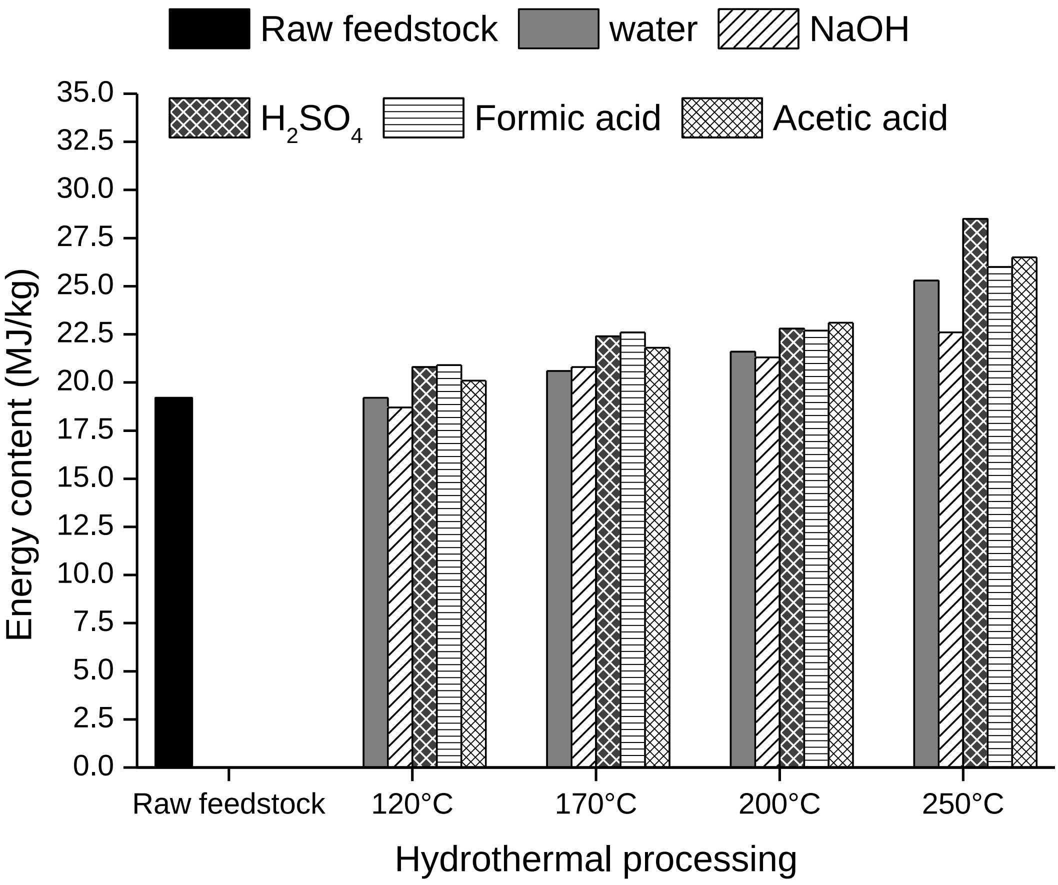


Figure 6-4: Comparing energy content in hydrochar/residues with unprocessed feedstock

6.3.2.4 Elemental analysis

Elemental analysis of the recovered solid products are presented in **Table 6-2**. A similar trend was observed with the elemental carbon as well in which higher processing temperatures (200 - 250°C) produced higher elemental carbon compared to the hydrochars from thermal hydrolysis. In particular, for both thermal hydrolysis and HTC, the hydrochars from the acidic additives had more elemental carbon than the neutral or basic additives. This observation agrees with the study by Reza et al., (2015) who conducted HTC on a different feedstock (wheat straw) using acetic acid and potassium hydroxide feedwater within pH 2 - 12 at 200°C and 260°C. They concluded that acidic feedwater used during HTC increased the elemental carbon in the hydrochar. Although they concluded that the strength of the basic feedwater did not affect elemental carbon during HTC, the results shown in **Table 6-2** indicates that both the neutral and basic additives increased the carbon content of the hydrochar compared to the unprocessed swine manure (46.4 %). They also concluded that although the acidic feedwater with pH 2 had the most carbon, the process temperature was a more dominant factor during HTC. Other effects of acidic pH feedwater on hydrochar products include larger surface area, pore volume and pore size compared to the hydrochars from basic feedwater with pH 12 (Reza et al., 2015).

Hydrogen content of the hydrochar at a specific thermal hydrolysis or HTC temperature was not affected by the feedwater pH; comparing both processes, the hydrogen in the HTC hydrochars were less than the amount present in the thermal hydrolysis hydrochars. It can be deduced that an increase in temperature reduces the elemental hydrogen in hydrochars. A similar observation was made by Reza et al., (2015). They compared the hydrogen content of hydrochars from 200°C and 260°C and concluded that process temperature has an obvious effect on the hydrogen content.

At any given temperature, nitrogen in the hydrochars reduced when compared to the nitrogen (3.0 %) in the unprocessed swine manure. This is likely as a result of nitrogen leaching into the aqueous phase during these processes and the formation of gases at higher processing temperatures. However within a particular set of processing temperature (mainly thermal hydrolysis at 120°C and 170°C), the hydrochar from the acidic feedwater had more nitrogen than the hydrochar from the neutral or basic feedwater. During HTC 200°C, the amount of nitrogen retained in the hydrochar was not affected by either the acidic, neutral and basic feedwater conditions as they were similar in the range of 2.3 - 2.4% which agrees with the study by Reza et al., (2015).

6.3.2.5 Effect on phosphorus concentration

Table 5-1 also shows the concentration of phosphorus in the unprocessed swine manure as 15580 mg kg^{-1} which is about 1.6 wt. %. **Table 6-2** also shows the extent of phosphorus retention in the hydrochar from this study. Generally, it was observed that the concentration of phosphorus retained in the hydrochar increased with processing temperature (120 - 250°C) under normal conditions with de-ionised water as well as with various additives. However the extent of P retention varied with each additive at any given temperature.

During thermal hydrolysis at 120°C, the concentration of phosphorus in the hydrochar was between 1.1 - 1.5% for de-ionised water, NaOH, formic acid and acetic acid but only 0.2% with H_2SO_4. During hydrolysis at 170°C, similar levels (2-2.2%) were obtained for most additives, with the least being 0.2% using H_2SO_4. During HTC, P retention in the hydrochars increased between 2.2-2.5% and 3.2-3.4% at 200°C and 250°C respectively. However using H_2SO_4 retained the least P at these temperatures; at 200°C and 250°C, concentration was 0.4% and 1.1% respectively.

Extracting phosphorus using mineral acid leaves the hydrochar with the least phosphorus content which is valuable as a fuel source. The residues with higher P retention are useful as a soil improver. However the phosphorus may not be bio-available.

6.4 Overall mass balance

Mass balance for nutrients and metals are presented in this section to give an insight on the fate of these nutrients and metals in the by-products after thermal hydrolysis and HTC. This is also an important factor to consider when deciding the potential application of these by-products (aqueous waste streams and hydrochar/residues) on a large scale. This information is significant in agriculture, as it helps to determine nutrient rich residues and hydrochars that are capable of enhancing crop yields. Also the fate of metals in the solid products will determine their suitability for crops and soil microbial population as only solid metal concentrations within the legal requirements are acceptable for land application in order to avoid toxicity.

6.4.1 Nutrient Distribution

6.4.1.1 Fate of nitrogen and phosphorus during thermal hydrolysis

Thermal hydrolysis at 120°C with de-ionised water and NaOH retained about 61-65% of the total nitrogen present in the unprocessed feedstock while with the acidic reagents, it was between 71 - 74% in the solid than in the aqueous product.

Phosphorus was mainly retained (63 - 84%) in the solid than in the aqueous product (11 - 30%) for most additives. With H_2SO_4, about 79% of the phosphorus was extracted, leaving 11% in the residue.

At 170°C, nitrogen was almost equally distributed between both products for all additives. Again phosphorus extraction was highest with H_2SO_4 (94%) leaving less than 6% in the residue. With other additives, most of the phosphorus (77 - 92%) was retained in the solid.

6.4.1.2 Fate of nitrogen and phosphorus during HTC

During HTC at 200°C and 250°C, nitrogen was almost equally distributed between the both products for all additives. Under normal conditions with water and alkali, phosphorus was almost completely retained (about 98%) and mainly present in the solid product using organic acids (86 - 87%). The least P in the solid was obtained using H_2SO_4 (17%) after extracting 80% into solution.

At 250°C, for most additives, phosphorus was still completely retained in the solid. However with H_2SO_4, it retained the least (36%).

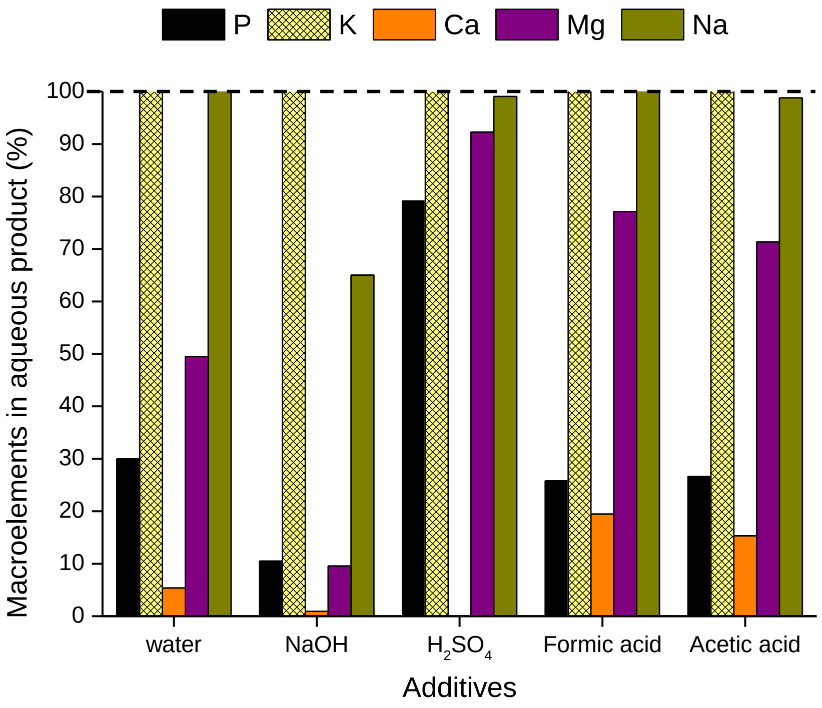
6.4.2 Metal Distribution

Although phosphorus has been included as part of the macronutrients in both products, its extraction and retention have been discussed in detail in the previous section. Therefore this section will focus mainly on metals.

6.4.2.1 Distribution of metals during thermal hydrolysis at 120°C

Figure 6-5 and **Figure 6-6** show the distribution of macronutrients into the aqueous and solid products respectively during thermal hydrolysis at 120°C.

Similar trends were observed for most elements. At this temperature, K and Na were completely extracted into solution for most additives. Although traces of these elements were present in the solid. This may be due to carry over during experimental analysis. With NaOH, Na was not completely extracted. Higher Na observed in the solid residue (25%). Using water, NaOH and organic acids, Ca is mostly retained (89-93%) in the solid with minimal extraction into the aqueous product. Generally the acidic reagents extracted higher levels of calcium into the aqueous product. Although calcium was not detected in the aqueous product from using H_2SO_4, the presence of calcium is suspected. Mg was mainly extracted (71-92%) using acidic reagents however it was equally distributed between both products using water. Most Mg with NaOH was present in the solid (84%) rather than in the aqueous product.



*120°C H2SO4 Calcium not detected, but calcium suspected

Figure 6-5: Extraction of macro elements in the aqueous product at 120°C

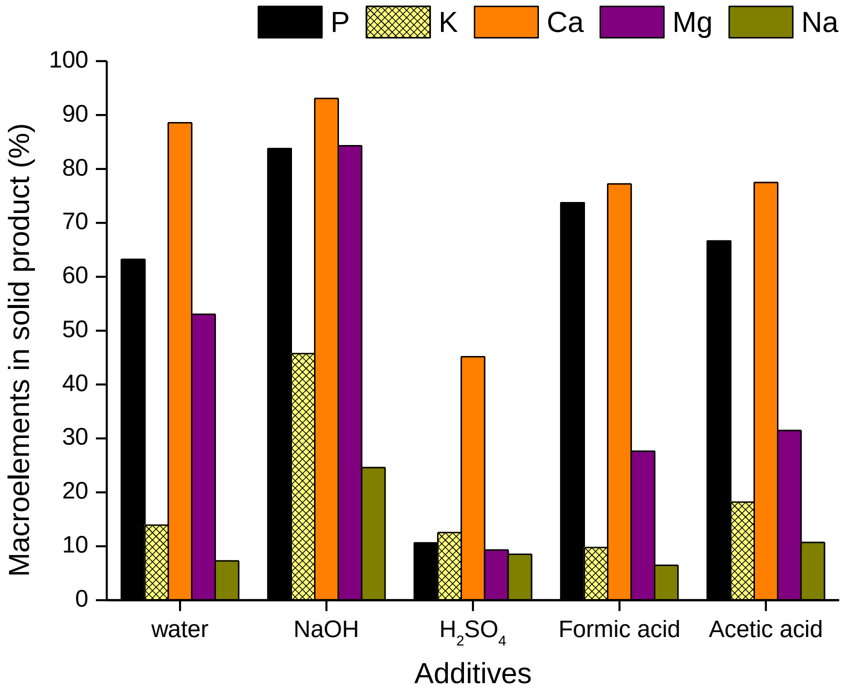


Figure 6-6: Retention of macro elements in the solid product at 120°C

Figure 6-7 and **Figure 6-8** show the distribution of micronutrients into the aqueous and solid products during thermal hydrolysis at 120°C.

At this temperature, the extraction of Fe into the aqueous product was particularly low between 2-9% for all additives. Fe is mainly retained in the solid product under normal conditions with water, alkali and organic acids (85-92%). However with H_2SO_4, low amounts of Fe was detected in the solid. Cobalt is mainly present in the solid (58- 73%) using water, NaOH and formic acid. Lower levels of Co in the solid was detected with H_2SO_4 and acetic acid. Higher Co extraction with acidic reagents compared with alkali conditions. H_2SO_4 still extracted the most (27%). Cu is mainly associated with the solid product (more than 71%) for all additives. Mn is mainly in the solid as well (more than 76%) for most additives except H_2SO_4. The acidic reagents extracted more Mn than water or NaOH, with H_2SO_4 extracting the most Mn (78%) leaving only 11% in the solid. Like Mn, Zn was also mainly in the solid (68-85%) for most additives except for H_2SO_4. Again the acidic reagents extracted more Zn compared to either water or NaOH, with H_2SO_4 extracting the most (55%).

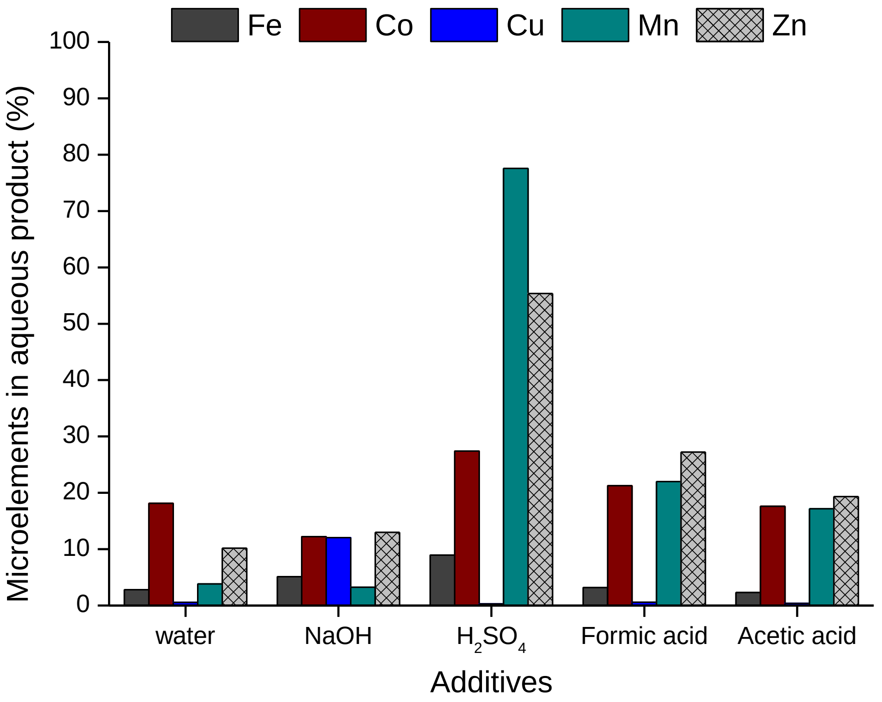


Figure 6-7: Extraction of micro elements in the aqueous product at 120°C

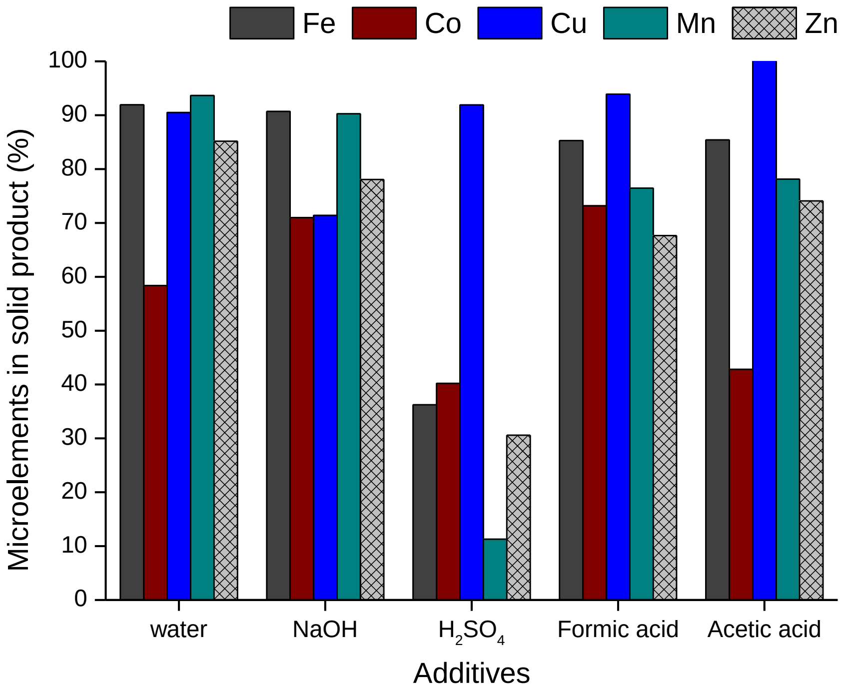


Figure 6-8: Retention of micro elements in the solid product at 120°C

6.4.2.2 Distribution of metals during thermal hydrolysis at 170°C

Figure 6-9 and **Figure 6-10** show the distribution of macronutrients into the aqueous and solid products during thermal hydrolysis at 170°C.

Similar trends were observed for most elements during thermal hydrolysis at 120°C and 170°C. Again K and Na were completely extracted into the aqueous product. Traces of these elements for the same reason as stated above. Ca is mostly present in the solid product (more than 78%) for most additives. However with H_2SO_4, Ca was equally distributed. Higher extractions of Ca with acidic reagents compared to either water or NaOH. H_2SO_4 extracted about 40% Ca, leaving 53% in the solid phase. Acid reagents generally extracted more Mg than NaOH. Higher Mg extraction (more than 78%) with organic acidic reagents and complete extraction with H_2SO_4. NaOH retained the most Mg (70%) followed by water.

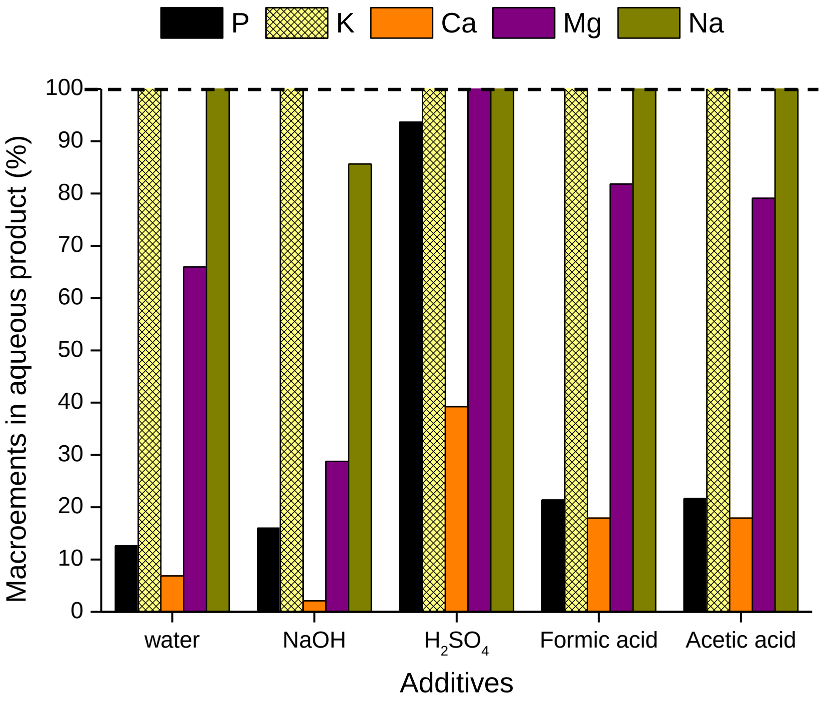


Figure 6-9: Extraction of macro elements in the aqueous product at 170°C

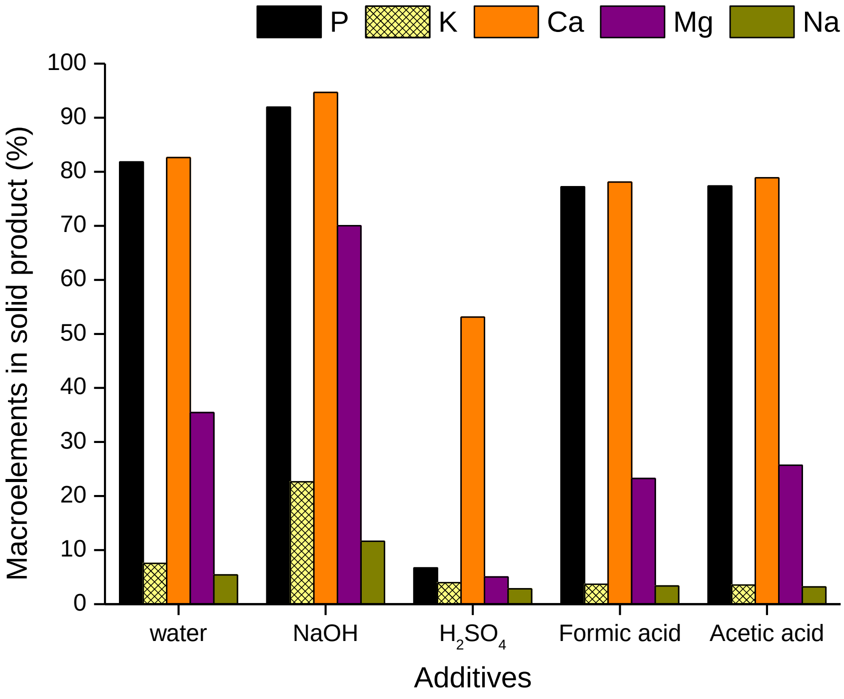


Figure 6-10: Retention of macro elements in the solid product at 170°C

Figure 6-11 and **Figure 6-12** show the distribution of micronutrients into the aqueous and solid products during thermal hydrolysis at 170°C.

At this temperature, Fe is mainly associated with the solid product (more than 70%) for most additives except H_2SO_4. Higher extraction of Fe in the aqueous products with acidic reagents. Although H_2SO_4 extracted the most Fe (27%). Co was equally distributed between these products for most additives. Cu was largely retained in the solid (82-96%). Mn also was mostly retained in the solid (more than 70%) for most of the additives except H_2SO_4. Higher extractions of Mn was mostly with acidic reagents with the highest extraction using H_2SO_4 (90%). Zn also was mainly present in the solid product (60-86%) for most additives except H_2SO_4. Again acidic reagents extracted the most Zn compared to water or NaOH. H_2SO_4 extracted the highest level of Zn (70%) while similar levels was observed with the organic acids.

Few heavy metals such as lead, nickel and aluminium were investigated in this study. Al levels in the aqueous products for both temperatures was less than 6% for most additives. Al was mainly present in the solid (more than 66%) for both temperatures. Ni extractions in aqueous product was less than 8% for most additives except for acetic acid which extracted 25%. Nickel in the solid was less than 22% for most additives except for acetic acid which retained 67% in the solid. Compared to Al and Ni, Pb was the most significant heavy metal. At 120°C, Pb was mainly extracted under normal conditions with water and NaOH (17-19%) and lower levels with acidic reagents (11-15%). However an increase in temperature to 170°C increased Pb extraction (25-33%) using water and NaOH. Higher Pb extraction were obtainable with temperature increase to 170°C; 41% using H_2SO_4 and 31-33% using the organic acids. Overall, more Pb concentrated in the solid than the aqueous product (63-72%) for most conditions.

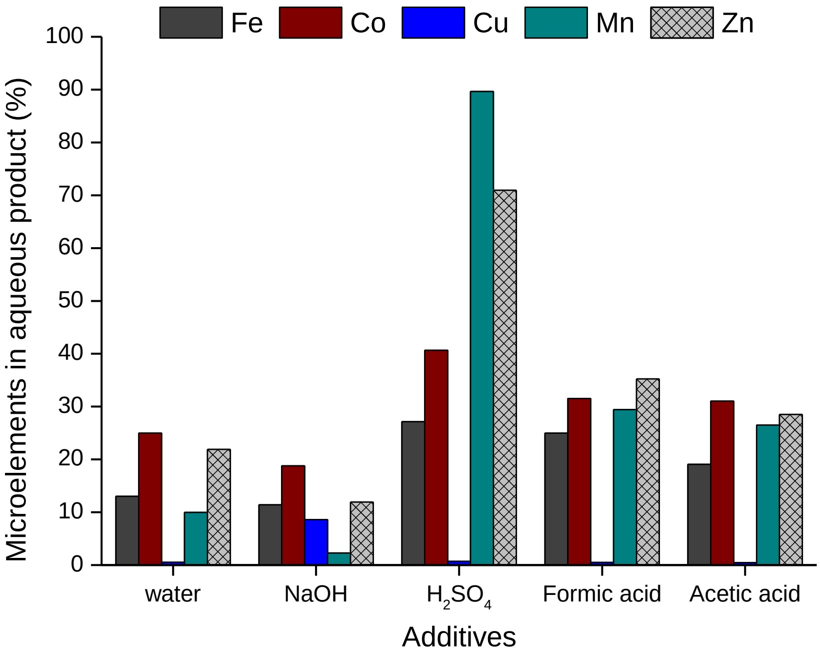


Figure 6-11: Extraction of micro elements in the aqueous product at 170°C

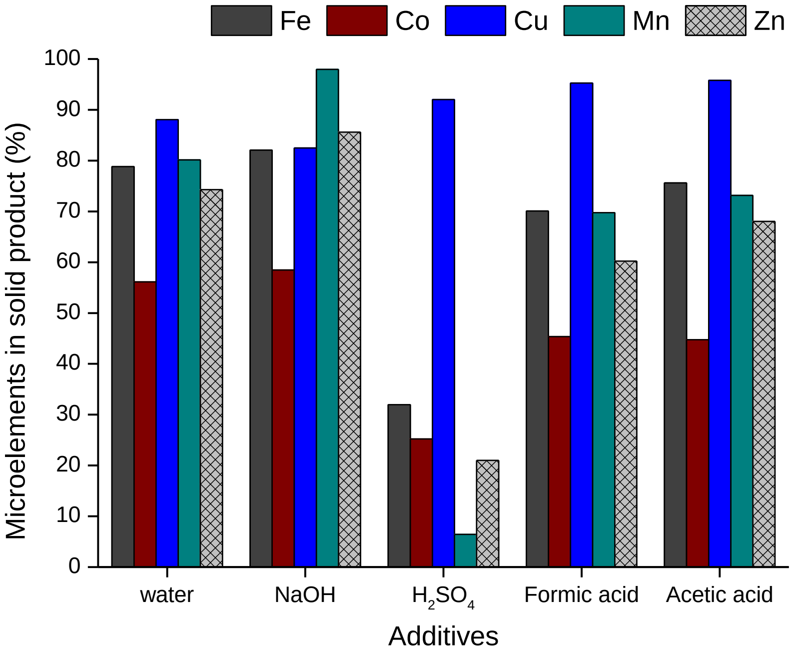


Figure 6-12: Retention of micro elements in the solid product at 170°C

6.4.2.3 Distribution of metals during HTC at 200°C

Figure 6-13 and **Figure 6-14** show the distribution of macronutrients into the aqueous and solid products during HTC at 200°C.

At this temperature, K and Na were mostly extracted into the aqueous product for all additives. Mg was mainly (more than 55%) in the aqueous phase as well. Acidic reagents extracted the most Mg compared to water or NaOH. Mg in the solid was higher with water and NaOH and lower with the acidic reagents. Ca was almost completely retained in the solid product for most additives (more than 85%) except for H_2SO_4. Higher Ca was extracted with the acidic reagents compared to water or alkali; H_2SO_4 extracted the most Ca (38%) whereas similar levels were extracted with organic acids.

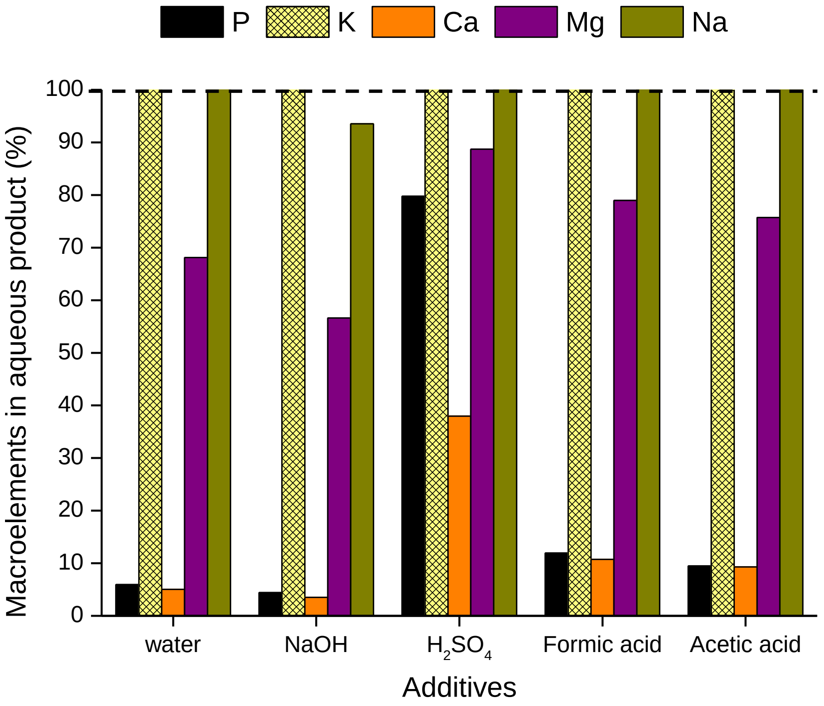


Figure 6-13: Extraction of macro elements in the aqueous product at 200°C

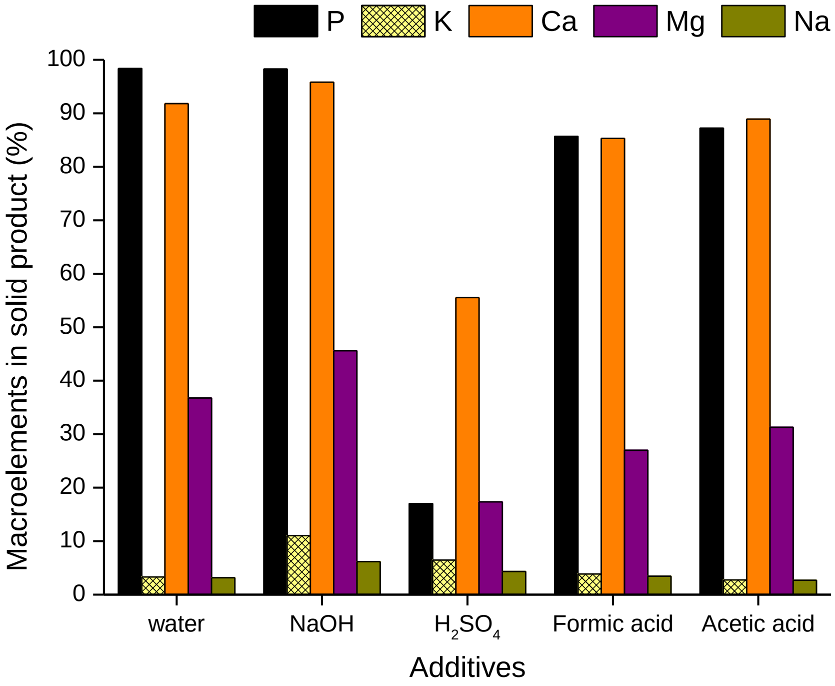


Figure 6-14: Retention of macro elements in the solid product at 200°C

6.4.2.4 Distribution of microelements during HTC at 200°C

Figure 6-15 and **Figure 6-16** show the distribution of micronutrients into the aqueous and solid products during HTC at 200°C.

Fe was retained mainly in the solid product (more than 65%) for most additives except for H_2SO_4. However Fe retention was higher with water and NaOH. The acidic reagents extracted more Fe than water or NaOH. H_2SO_4 extracted the most Fe (29%) and lower levels with the organic acids (18-21%). Cobalt was mainly retained in the solid than in the aqueous product. Higher Co levels were observed with water (83%) and lower retention levels was observed with the other additives (34-50%). Like Fe, acidic reagents extracted more cobalt (29-39%) than water or NaOH. Cu was completely associated with the solid product for all conditions with levels ranging from 93-96%. Also Mn is mainly associated with the solid (78-82%) except for H_2SO_4. Extraction of Mn was higher with the acidic reagents than with water or NaOH, with the highest extraction with H_2SO_4 (73%) and similar levels with organic acids (19-21%). Zn was mainly in the solid as well with levels more than 65% for most additives except H_2SO_4. Again the acidic reagents extracted more Zn than water or NaOH. The highest level of Zn was extracted with H_2SO_4 (63%).

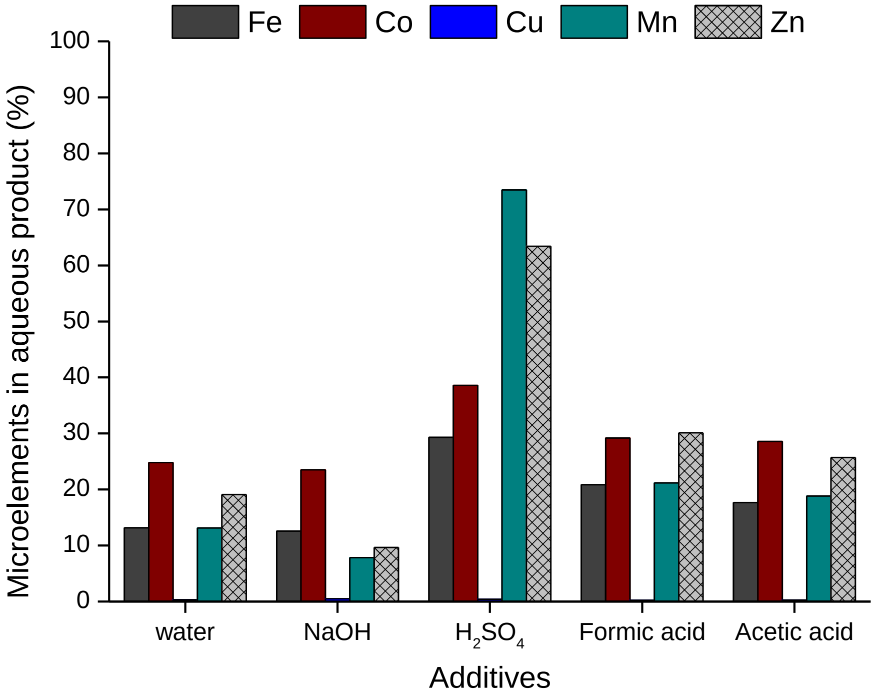


Figure 6-15: Extraction of micro elements in the aqueous product at 200°C

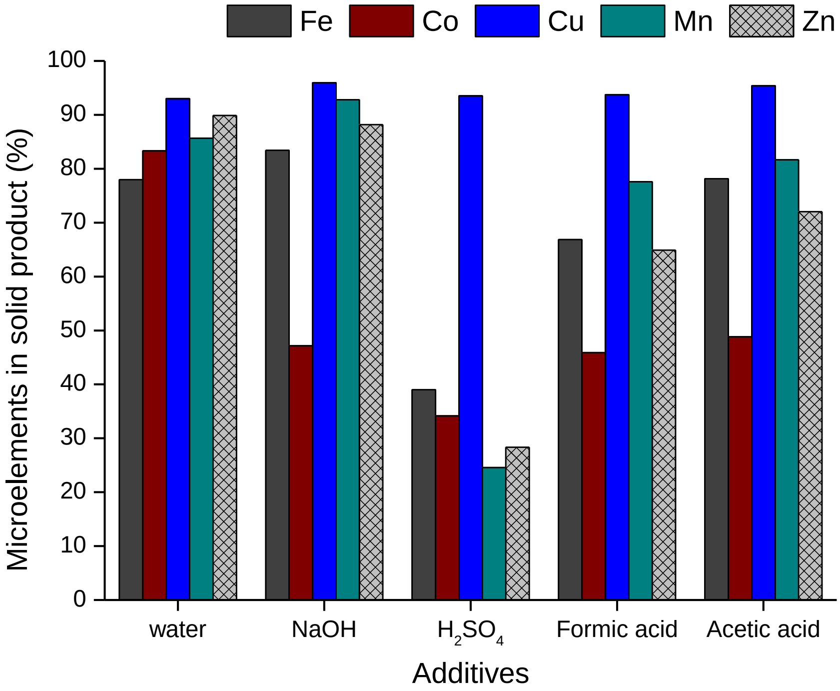


Figure 6-16: Retention of micro elements in the solid product at 200°C

6.4.2.5 Distribution of metals during HTC at 250°C

Figure 6-17 and **Figure 6-18** show the distribution of macronutrients into the aqueous and solid products during HTC at 250°C.

At this temperature, K and Na were also completely extracted into the aqueous product for all additives. Mg is mainly extracted in the aqueous product using acidic reagents and water (55-68%), although the levels have reduced considerably compared to HTC 200°C. Mg is retained the most in the solid using NaOH (58%). Ca concentrates in the solid for most additives (more than 87%) except H_2SO_4. Although H_2SO_4 extracted the most Ca (37%) compared to other additives.

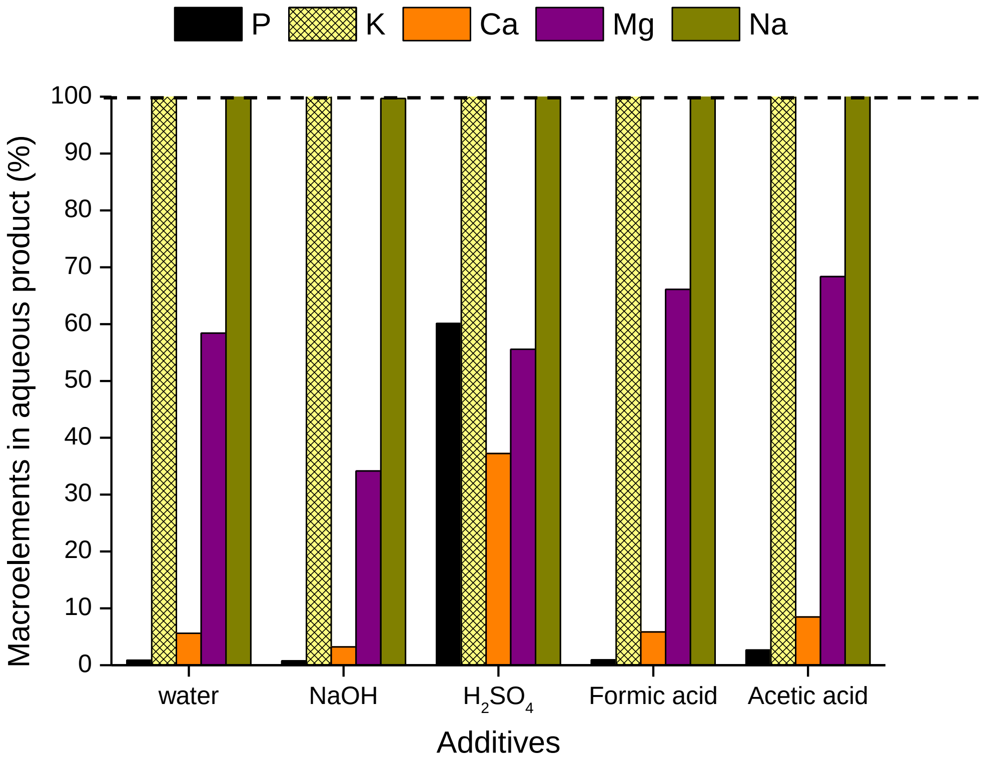


Figure 6-17: Extraction of macro elements in the aqueous product at 250°C

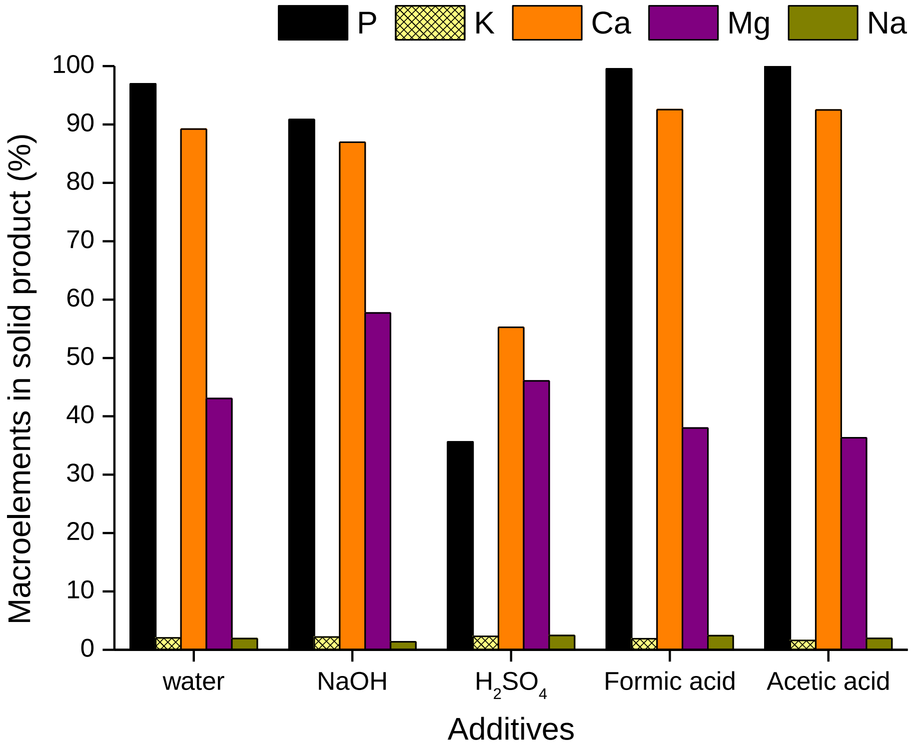


Figure 6-18: Retention of macro elements in the solid product at 250°C

Figure 6-19 and **Figure 6-20** show the distribution of micronutrients into the aqueous and solid products during HTC at 250°C.

At this temperature, Fe is mainly retained in the solid between 68-87% for most additives; with H_2SO_4, Fe retained was the lowest. The aqueous products had less than 3% Fe for most additives however with H_2SO_4, about 10% Fe was extracted. Also H_2SO_4 extracted the highest Co (26%). Comparing HTC 200°C to 250°C, cobalt extraction reduced significantly with increasing temperature. Similar levels of Co (50-56%) was retained in the solids for all additives. Cu was mainly in the solid as well (85-96%) and not extracted at all into the aqueous phase. Mn also was mainly associated with the solid with levels between 85-92% for most additives although with H_2SO_4, the levels were slightly lower. Generally low levels of Mn was in the aqueous product, however the most Mn was extracted with H_2SO_4 (43%). Zn was also mainly in the solid with levels between 85-96% for most additives, but lower levels were observed with H_2SO_4 (68%). Very little amount of Zn was extracted into the aqueous product (2-3%); although the highest Zn was extracted with H_2SO_4 (28%).

At both temperatures, very low extractions of Ni was observed in the aqueous product using all additives. The solid products had Ni between 21-33%. At 200°C, low levels of Al was extracted (less than 2%) for most additives although with H_2SO_4, Ni was 7%. Al levels in the aqueous product decreased with increasing temperature to 250°C. With most additives, Al was not present in the aqueous product, but reduced with H_2SO_4 (4%). At 200°C, Al was mainly retained in the solid (67-78%) for most additives, but was completely retained in the solid with NaOH (97%). At 250°C as well, Al was mainly in the solid product for most additives. Pb extraction was mostly extracted with acidic reagents with levels between 37-53%. Extraction of Pb into the aqueous products was higher during thermal hydrolysis than HTC. At 250°C, even with the acidic reagents, Pb extraction reduced by 3-6%. At both temperatures, Pb in the solid product was between 68-82% for most additives while it was lower 48-64% with H_2SO_4.

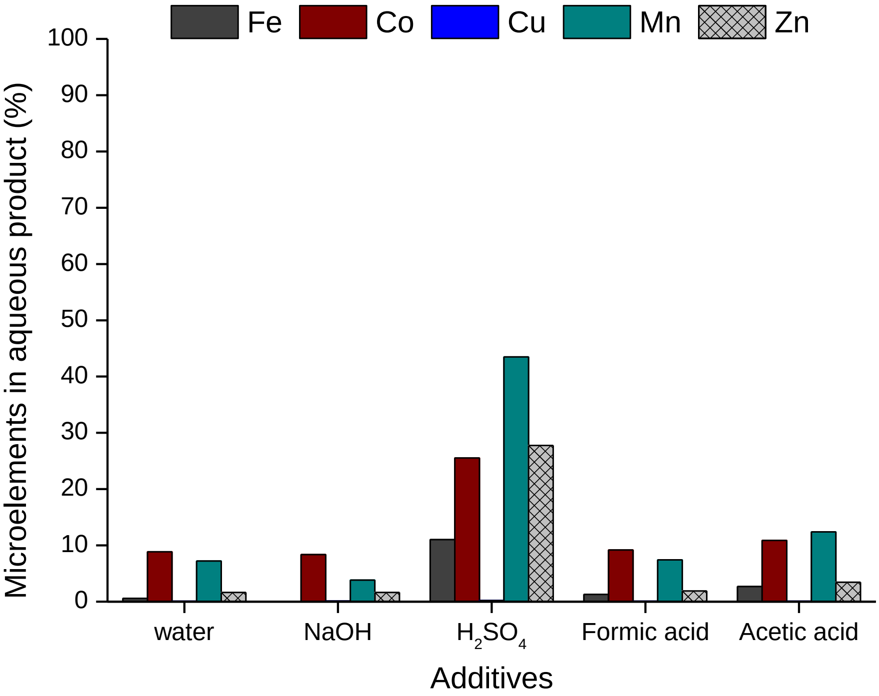


Figure 6-19: Extraction of micro elements in the aqueous product at 250°C

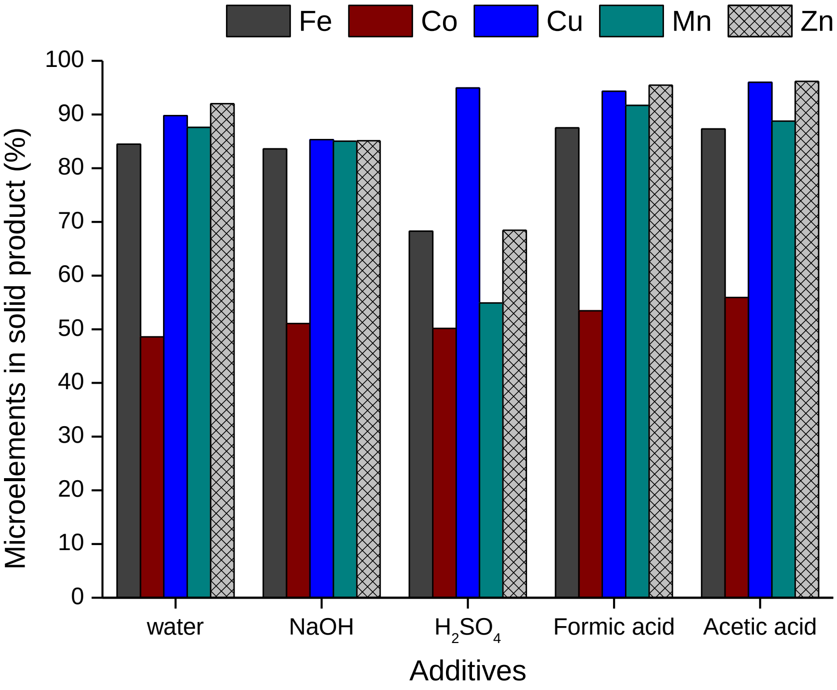


Figure 6-20: Retention of micro elements in the solid product at 250°C

Generally acidic reagents generally extracted more metals into the aqueous phase compared to the levels extracted under neutral or alkali conditions. This is the reason for the low ash contents in the recovered solid products from acid treatment as discussed in **Section 6.3.2.1**.

6.5 Conclusion

Na and K were completely extracted into the aqueous products at the lowest temperature (120°C) and this was certainly the case at higher temperatures. Mg extraction into the aqueous product peaks at 170°C, and afterwards reduces with increasing temperature from 200-250°C. Ca extraction into the aqueous product is enhanced at lower pH. Acidic reagents extracted more Ca than neutral or alkali reagents. Although higher extractions with H_2SO_4 as organic acids had similar performance. Overall, Mg, Na and K were mostly present in the aqueous product while Ca, P was mainly in the solid product. Ca concentrates in the solid product as temperature increases from 120-250°C.

For most additives, most micronutrients were mainly in the solid product except for Mn and Zn which were mostly extracted into the aqueous product using H_2SO_4. Extraction of Mn and Zn with H_2SO_4 peaks at 200°C, and concentrates in the solid at higher temperature (250°C). Generally, higher levels of micronutrients were extracted with acidic reagents compared to water or NaOH. Extraction of Mn and Zn with organic acids is similar.

Increasing temperature from 120-250°C, did not increase the levels of Fe, Co, Cu. For Mn, increase in temperature increased its levels in the solid product especially for acidic reagents, but reduced in neutral or alkali conditions.

During thermal hydrolysis, very low Al (<6%) in aqueous product for most additives. Al mainly in the solid product. Ni levels were also very low (<8%) in the aqueous products from most additives, although with acetic acid significant extraction was observed. Generally Ni was more in the solid product. For instance with acetic acid, it was 67%. Pb extraction was <20% in the aqueous product for all additives although higher levels under neutral and alkali conditions. Increasing temperature to 170°C, increased Pb extraction; 25-33% under neutral and alkali conditions and 41% with H_2SO_4 and 31-33% with organic acids. Generally during thermal hydrolysis, Pb was mainly retained in the solid products for all additives.

During HTC, very low Ni extractions into the aqueous product as well. In solid, low levels of Ni were observed (21-33%). At 200°C, also very low Al extractions (<7%) for most additives. Increase in temperature to 250°C reduced Al extractions. Generally Al is mainly in the solid product (67-78%) for most additives, but completely retained with NaOH. During HTC, Al is mainly associated with the solid product than the aqueous product. The presence of Pb in the aqueous product is more significant than Al or Ni. Higher Pb extractions with acidic reagents while Pb extraction reduced with increase in temperature to 250°C. Generally Pb is associated more with the solid products at higher temperatures; 68-82% for most additives and 48-64% with H_2SO_4.

Chapter 7 A comparison of nutrient extraction using microwave and conventional heating during thermal hydrolysis

7.1 Introduction

In **Chapter 4**, **Chapter 5** and **Chapter 6**, hydrothermal processing of biomass was by conventional heating method. However in this chapter another type of heating – microwave heating was applied during hydrothermal processing of biomass so as to investigate the effect of heating types on nutrient extraction. Microwave extraction was performed using five feedstocks- Sewage sludge, *Chlorella vulgaris*, digestate, swine manure and chicken manure. Sewage sludge was included as an additional feedstock in order to determine any differences between untreated sewage sludge and 'treated' digestate. It was not possible to include sewage sludge in earlier work as the sample was not available.

Pre-treatment of these feedstocks with de-ionised water using microwave heating was performed at a lower temperature (120°C) and shorter residence time (15 minutes). Lower temperature extraction was found previously to extract higher amounts of phosphorus. The product yields, aqueous and solid product composition, nitrogen extraction, phosphorus extraction, metal extraction, the distribution of these nutrients and metals between the solid and aqueous products were investigated.

Also, pre-treatment of swine manure was performed using microwave heating at 120°C for 15 minutes in the presence of the various additives (alkali – 0.1M sodium hydroxide, mineral acid- 0.1M sulphuric acid and the organic acids, 0.1M acetic acid and 0.1M formic acid). The aim of this study was to investigate the possibility of enhancing nitrogen and phosphorus extraction at lower temperature (120°C) and shorter residence time (15 minutes) using microwave heating. Also the product yields, aqueous and solid product composition, nitrogen extraction, phosphorus extraction, metal extraction, the distribution of these nutrients and metals between the solid and aqueous products using these additives were investigated. The levels of nutrients extracted with these additives using the microwave heating were compared to the nutrient extraction results obtained with the same additives using conventional heating in a Parr reactor at 120°C for 60 minutes (Results are presented in **Chapter 5**).

Detailed methodology of the experimental setup and analytical methods used for the solid and aqueous products are described in **Chapter 3**.

7.2 Characterisation of feedstock

7.2.1 Proximate and ultimate analyses

The feedstocks used for the various hydrothermal processes were analysed for moisture, ash, volatiles and fixed carbon as well as the elemental composition as stated in **Chapter 3**. The results are shown in **Table 7-1** and include an additional fifth feedstock, in this case, sewage sludge. The results are slightly different from those described in **Table 4-1** as it includes characterisation of sewage sludge**.**

The feedstocks generally have high ash contents with similar levels for the manures (10.9-12.7 wt%) followed by sewage sludge (21.3 wt%) with the highest being the digestate. Most of the feedstocks have high volatile content between 61.1-82.7 wt% however the digestate is considerably lower (34.4 wt%) as it has been previously treated by anaerobic treatment and is high in ash. The microalgae has the highest nitrogen content (9.7 wt. %) followed by sewage sludge and chicken manure which contain similar amounts (5.2-5.7 wt%). The nitrogen in the digestate and swine manure were the lowest. The proportion of sulphur in all the feedstocks was less than 0.9%. For which contains significantly less carbon (18.3 wt%). This reduction in carbon is due to the high levels of ash following anaerobic treatment. The energy content for most of the feedstock was in the range 18.3-21.1 MJ kg^{-1} with the exception of digestate which was significantly lower at 7.8 MJ kg^{-1}.

Table 7-1: Proximate and ultimate analyses of various feedstocks investigated

	Proximate analyses (%)				Ultimate analyses[a] (%)					
	Moisture	Ash [a]	Volatiles	Fixed carbon	C	H	N	S	O[b]	HHV
Biomass										(MJ kg^{-1})
Sewage sludge	4.0	21.3	70.9	4.7	41.0	6.3	5.2	0.8	25.5	18.4
Chlorella vulgaris	3.4	9.8	82.7	4.5	46.8	6.9	9.7	0.5	26.3	21.1
Digestate	2.9	61.2	34.4	3.3	18.3	2.9	2.7	0.3	14.6	7.8
Swine manure	5.3	12.7	61.1	21.6	46.4	6.3	3.0	0.2	31.4	19.2
Chicken manure	5.6	10.9	62.7	21.5	43.9	6.5	5.7	0.2	32.8	18.3

[a] dry basis

[b] Calculated as difference between sum of C,H,N,S, ash

Table 7-2: Nutrient and metal in the feedstocks investigated (dry basis)

Biomass	Concentration (mg kg^{-1})												
	P	**K**	**Ca**	**Mg**	**Na**	**Fe**	**Al**	**Ni**	**Co**	**Cu**	**Pb**	**Mn**	**Zn**
Sewage sludge	10,690	4,610	13,660	3,830	1,270	16,050	14,100	20	5.7	150	80	930	420
Chlorella vulgaris	18,730	9,150	14,480	5,960	1,680	3,390	2,390	2	0.9	3	7	110	60
OWS Digestate	13,890	9,070	20,880	6,480	1,070	35,600	20,530	20	7.2	220	129	250	820
Swine manure	15,580	12,120	31,690	9,240	3,030	1,050	480	30	1.0	160	2.4	370	690
Chicken manure	10,800	29,400	16,420	7,000	3,230	510	220	2	0.4	100	2.1	490	360

[*] Analysis by ICP-OES

7.2.2 Metal composition

Table 7-2 shows the nutrient and metal composition of the feedstocks processed by microwave hydrothermal pre-treatment. *Chlorella* has the highest level of phosphorus (18,730 mg kg^{-1}) followed by swine manure (15,580 mg kg^{-1}). All the other feedstocks have levels of phosphorus between 10,690-13,890 mg kg^{-1}. The manures have a higher potassium content than other feedstocks, chicken manure has the most potassium (29,400 mg kg^{-1}) followed by swine manure with 12,120 mg kg^{-1}. *Chlorella*, digestate and sewage sludge have potassium in the range 4,610-9,150 mg kg^{-1}. Calcium was high in all the feedstocks and about 20,880-31,690 mg kg^{-1} in digestate and swine manure while it was between 13,660-16,420 mg kg^{-1} for sewage sludge, *Chlorella* and chicken manure. Similar magnesium levels was present in chlorella, digestate and chicken manure, but highest with swine manure (9,240 mg kg$^{-\ 1}$). In all feedstocks, sodium was between 1,070-3,230 mg kg^{-1}. Iron and aluminium was particularly high both in sewage sludge and digestate with levels being 16,050 mg kg^{-1} and 14,100 mg kg^{-1} respectively for sewage sludge, 35,600 mg kg^{-1} and 20,530 mg kg^{-1} respectively for digestate. Iron and aluminium was lowest in chicken manure having about 510 mg kg-^{1} and 220 mg kg$^{-\ 1}$ respectively. Copper and lead were particularly low in the microalgae having 3 mg kg^{-1} and 7 mg kg^{-1} respectively.

7.3 Microwave hydrothermal Pre-treatment

7.3.1 Solid yields

The major products obtained after the microwave pre-treatment process are the solid residues and water soluble products in the aqueous phase. Under normal conditions with de-ionised water as shown in **Figure 7-1**, the highest solid yield (83 - 86%) was obtained with digestate followed by 71 - 81% was obtained with sewage sludge and swine manure. About 69 - 71% solid was obtained from microalgae feedstock while the lowest yield (54%) was obtained with chicken manure. As shown in **Figure 7-2**, the use of additives during the microwave pre-treatment process had similar solid yields especially with acetic acid and NaOH having between 75-77%. However slightly lower yields were obtained with formic acid (71-72%) but the lowest yield (49-63%) was with H_2SO_4.

^{CM} Chicken manure ^{SS} Sewage sludge ^{SM} Swine manure

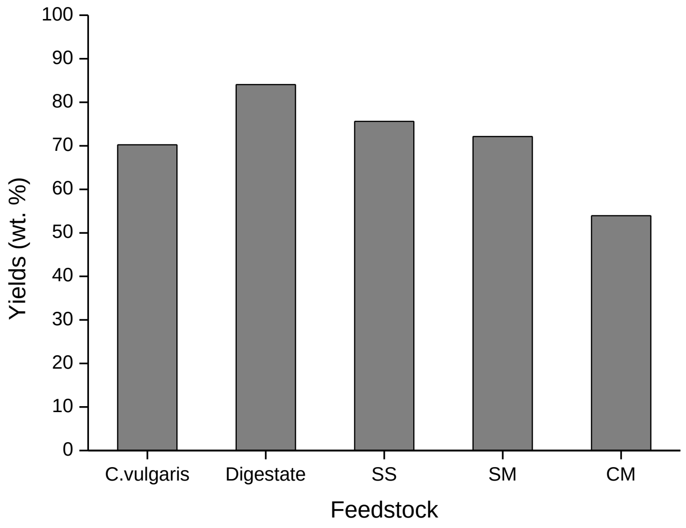


Figure 7-1: Solid yield from microwave processing of various feedstocks

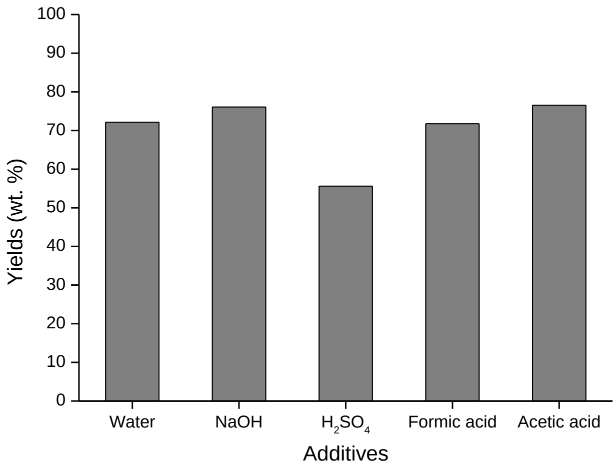


Figure 7-2: Solid yield from microwave processing of swine manure with additives

7.3.2 Characterisation of the solid product

7.3.2.1 Proximate and ultimate analyses

The solid products obtained after microwave pre-treatment under normal conditions were analysed also for moisture, ash, volatiles and fixed carbon as well as the elemental composition as stated in **Chapter 3** and the results are shown in **Table 7-3**.

Most of the residues have high carbon content between 44.1-51.9 wt% and an energy content between 19.5-24.9 MJ kg^{-1} with the exception of the residues from digestate which had lower carbon (15.3 wt %) and result in the lowest energy content of 6.6 MJ kg^{-1}. The proportion of ash in the residue from digestate and sewage sludge were particularly high compared to the residues from the other feedstocks having about 68.3 wt % and 27.0 wt % respectively. The ash in the residues from microalgae, swine manure and chicken manure were lower and between 8.5-9.8 wt %. The residues from the microalgae had the highest volatile content (82.3 wt %), followed by sewage sludge which was 65.7 wt%. Residues from the manures had similar volatile content between 61.6 - 64.1 wt % while the digestate had the least volatile content 26.7 wt%. The residues from sewage sludge and chicken manure had similar nitrogen between 5.2-5.7 wt% while nitrogen in the residues from digestate and swine manure were also similar between 2.7-3.0 wt %. *Chlorella* residue had the highest nitrogen (9.7 wt %). Sulphur was very low in all residues ranging from 0.2-0.7 wt%.

Table 7-4 lists the moisture, ash, volatiles and fixed carbon as well as the elemental composition of microwave hydrothermal pre-treated residues using additives. The carbon content in most of the residues were between 49.3-50.7 wt %, however with NaOH it was slightly lower at about 46.5 wt %. Most of the residues using additives had similar nitrogen content in the range 2.6-3.0 wt% with the exception of with NaOH, which was slightly lower (2.3 wt%). Sulphur was about 0.3 wt% for most of the residues using additives except for H_2SO_4 which had higher sulphur content (1.1%). The highest ash content (13.8 wt %) was with NaOH followed by the residue using de-ionised water which was 9.8 wt %. The residues with the acidic reagents had lower ash contents 5.3 wt %, 6.8 wt % and 8.1 wt % using H_2SO_4, formic acid and acetic acid respectively. The volatile content in the residues were higher using the acidic reagents (63.6-66.3 wt%) compared to the residues using de-ionised water (61.6 wt%) and NaOH (60.5 wt%). **Table 7-4** also lists the higher heating values (HHV) of the swine manure residues using additives. There was little change in HHV and was between 19.7-21.4 MJ kg^{-1}.

Table 7-3: Proximate, ultimate analyses and HHV of residues from microwave hydrothermal pre-treatment in water alone

Conditions	Moisture	Ash [a]	Volatiles	Fixed carbon	C	H	N	S	O[b]	HHV (MJ kg^{-1})
	Proximate analyses (%)				**Ultimate analyses[a] (%)**					
Sewage sludge	3.4	27.0	65.7	4.9	44.1	6.6	4.7	0.5	17.0	21.4
Chlorella vulgaris	4.1	8.6	82.3	5.4	51.9	7.7	10.3	0.7	20.9	24.9
Digestate	3.7	68.3	26.7	3.8	15.3	2.5	1.8	0.2	11.8	6.6
Swine manure	6.0	9.8	61.6	23.4	49.3	6.8	2.6	0.3	31.3	20.9
Chicken manure	4.5	8.5	64.1	23.4	46.8	6.7	4.5	0.2	33.3	19.5

[a] dry basis

[b] Calculated as difference between sum of C,H,N,S, ash

Table 7-4: Proximate, ultimate analyses and HHV of swine manure residues from microwave pre-treatment using additives

	Proximate analyses (%)				**Ultimate analyses[a] (%)**					
Biomass	Moisture	Ash [a]	Volatiles	Fixed carbon	C	H	N	S	O[b]	HHV (MJ kg^{-1})
De-ionised water	6.0	9.8	61.6	23.4	49.3	6.8	2.6	0.3	31.3	20.9
NaOH	5.5	13.8	60.5	21.1	46.5	6.5	2.3	0.3	30.6	19.7
H_2SO_4	2.8	5.3	66.3	25.8	50.2	6.7	2.8	1.1	33.8	20.6
Formic acid	4.1	6.8	64.8	24.7	50.7	7.0	2.8	0.3	32.4	21.4
Acetic acid	4.1	8.1	63.6	24.6	49.7	6.8	3.0	0.3	32.1	20.9

[a] dry basis

[b] Calculated as difference between sum of C,H,N,S, ash

7.3.2.2 Nutrients and metals present in the residues

Table 7-5 lists the nutrient and metal content of the processed residues from the microwave hydrothermal pre-treatment of the five feedstocks.

In all the residues, the phosphorus increases after pre-treatment resulting in similar concentrations in the manures and sewage sludge (11,020-12,240 mg kg^{-1}) although higher concentrations were observed in the residues from digestate (16,660 mg kg^{-1}) and microalgae (18,720 mg kg^{-1}). The residue from the chicken manure had the most potassium (8,010 mg kg^{-1}) but this was significantly reduced compared to the feedstock which had 29,400 mg kg^{-1}. With the concentration of potassium in the swine manure residue was less (2,720 mg kg^{-1}) compared to 12,120 mg kg^{-1} in the unprocessed feedstock. Similar concentrations of potassium were present in the residues from sewage sludge, microalgae and swine manure having between 2,040-3,440 mg kg^{-1}. Sodium in the residues reduced as well compared to the feedstocks. In particular the manures readily released sodium changing the concentration from about 3,030-3,230 mg kg^{-1} to about 610-770 mg kg^{-1} in the residues. Unlike potassium and sodium Calcium was more concentrated in the residues compared to the unprocessed feedstocks. Calcium was most concentrated in the residue from chicken manure having 27,490 mg kg^{-1} compared to the feedstock (16,420 mg kg^{-1}). Magnesium reduced in all the residues compared to the feedstock. Most of the residues had similar concentration of magnesium ranging between 5,200-6,670 mg kg^{-1} except for sewage sludge with the least 3,580 mg kg^{-1}. The immobilisation of phosphorus in the residues is likely to be linked to the increased levels of Calcium and magnesium in the residues. Iron also concentrated in the residues during the pre-treatment process. The residues from sewage sludge and digestate contain the highest iron content, 21,250 mg kg^{-1} and 41,390 mg kg^{-1} respectively. However this is mainly as a result of the high iron content originally present in the feedstock (16,050 and 35,600 mg kg^{-1} respectively). Aluminium was also concentrated in most residues except for digestate and swine manure which had relatively constant levels of Al even after pre-treatment. Ni, Co, Mn and Zn were concentrated in the residue although the levels in the residues are low compared to other metals.

Table 7-6 lists the nutrient and metal content of the processed residues from the microwave pre-treatment of swine manure using alkali, mineral acid and organic acids. Phosphorus is concentrated more in the residue following treatment in alkali, however it reduces slightly with de-ionised water. Generally the acidic reagents result in less phosphorus in the residue. Phosphorus was lowest following treatment in H_2SO_4 (2,480 mg kg^{-1}) and higher in the residues treated with organic acids. Using the additives, potassium reduces significantly in the residues. With alkali and de-ionised water, calcium increased in the residues, however with the acidic reagents, there was a reduction in calcium (18,610-27,210 mg kg^{-1}). Magnesium generally reduced with de-ionised water and the acidic reagents most especially with H_2SO_4 (1,520 mg kg^{-1}) however with NaOH, it increased (11,061 mg kg^{-1}). Like magnesium, sodium behaves in a similar manner. Iron increases in most of the residues with similar concentrations between 1240-1330 mg kg^{-1} except with H_2SO_4 with the least iron (416 mg kg^{-1}). The use of additives have no significant effect on the concentration of aluminium, cobalt, copper and lead in the residues after pre-treatment. Nickel in the residues was between 8-13 mg kg^{-1}. Manganese and zinc increased with de-ionised water and NaOH to 420-430 mg kg^{-1} and 758-778 mg kg^{-1} respectively. With acidic reagents, manganese and zinc reduced particularly with H_2SO_4 which had 53 and 140 mg kg^{-1} respectively.

Table 7-5: Nutrients and metals in the residues from microwave pre-treatment using de-ionised water (dry basis)

Conditions	Concentration (mg kg^{-1})												
	P^{a}	K^{b}	Ca^{b}	Mg^{b}	Na^{b}	Fe^{b}	Al^{b}	Ni^{b}	Co^{b}	Cu^{b}	Pb^{b}	Mn^{b}	Zn^{b}
Sewage sludge	11,510	3,440	14,830	3,580	430	21,250	15,910	30	6.2	210	80	1,120	560
Chlorella vulgaris	18,720	2,040	17,890	5,800	440	3,930	3,020	10	1.3	6	4	160	80
Digestate	16,660	5,920	24,280	6,660	430	41,390	19,840	20	7.0	250	110	340	940
Swine manure	12,240	2,720	33,930	6,670	610	1,240	410	8	0.6	180	3	420	760
Chicken manure	11,020	8,010	27,490	5,200	770	630	420	4	0.7	180	1.1	810	530

[a] Analysis by colorimetry
[b] Analysis by ICP-OES

Table 7-6: Nutrients and metals in the swine manure residues from microwave pre-treatment using additives (dry basis)

Conditions	Concentration (mg kg^{-1})												
	P[a]	K[b]	Ca[b]	Mg[b]	Na[b]	Fe[b]	Al[b]	Ni[b]	Co[b]	Cu[b]	Pb[b]	Mn[b]	Zn[b]
De-ionised water	12,240	2,720	33,930	6,670	610	1,240	410	8	0.6	180	3	420	760
NaOH	15,960	4,360	37,210	11,060	11,030	1,290	430	8	1.2	140	3	430	780
H_2SO_4	2,480	1,820	18,610	1,520	470	420	420	10	0.6	190	1	50	140
Formic acid	9,250	1,860	20,430	2,900	450	1,250	420	10	0.8	190	2	260	510
Acetic acid	11,200	2,040	27,210	3,790	490	1,330	450	10	0.8	190	2	340	630

[a] Analysis by colorimetry

[b] Analysis by ICP-OES

7.3.3 Characterisation of the aqueous product

7.3.3.1 pH

The pH of the aqueous phase recovered after microwave hydrothermal pretreatment of the different feedstock in water alone is shown in **Table 7-7**. Generally the aqueous products were acidic in nature for all feedstocks. The aqueous products from sewage sludge, *C.vulgaris* and the manures had similar pH in the range 5.1-5.5 with the exception being digestate which had a slightly higher pH at 6.5. The pH of the process waters using reagents is shown in **Table 7-8** and results in a reduction in the pH of the aqueous products to less than 2 using H_2SO_4 and between 4.1-4.6 using the organic acids compared to normal conditions with water which is pH 5.3. The pH of the aqueous product recovered after using NaOH is alkaline (pH 9.7) which will favour phosphorus precipitation in the residue and less will be extracted into solution.

Table 7-7: pH, total organic carbon (TOC), nitrogen and phosphorus in the aqueous products using de-ionised water

		Concentration (mg kg^{-1})			
Conditions	pH	TOC	Total N	Total P	Total K
Sewage sludge	5.1	67,080	16,240	2,830	1,580
C.vulgaris	5.3	75,160	25,180	7,220	7,090
Digestate	6.5	37,240	11,990	1,280	2,750
Swine manure	5.3	51,350	11,390	4,560	11,220
Chicken manure	5.5	116,590	11,480	10,580	24,050

*pH values ± 0.4

Table 7-8: pH, total organic carbon (TOC), nitrogen and phosphorus in the aqueous products from swine manure using additives

		Concentration (mg kg^{-1})			
Conditions	pH	TOC	Total N	Total P	Total K
De-ionised water	5.3	51,350	11,390	4,560	11,220
NaOH	9.7	79,300	12,540	2,100	9,980
H_2SO_4	< 2	110,300	14,020	13,010	12,400
Formic acid	4.1	70,210	9,660	6,740	12,130
Acetic acid	4.6	80,600	6,760	5,250	11,820

*pH values ± 0.4

7.3.3.2 Total organic carbon (TOC)

The concentrations of TOC in the aqueous phase recovered after microwave hydrothermal processing of the different feedstocks in water alone is shown in **Table 7-7**. The highest levels of TOC were found in the aqueous product from chicken manure (116,590 mg kg^{-1}), followed by *C.vulgaris* (75,160 mg kg^{-1}), sewage sludge (67,080 mg kg^{-1}) then swine manure (51,350 mg kg^{-1}). The lowest TOC was in the aqueous product from digestate (37,240 mg kg^{-1}).

The use of additives in microwave hydrothermal pre-treatment of swine manure are shown in **Table 7-8** and indicated an increase in the TOC levels in the aqueous products compared to normal conditions with water alone (51,350 mg kg^{-1}). The highest TOC was observed with H_2SO_4 (110,300 mg kg^{-1}). Similar TOC was observed with NaOH and acetic acid having concentration between 79,300 - 80,600 mg kg^{-1}. However with formic acid it was lower (70,210 mg kg^{-1}).

7.3.3.3 Distribution of nitrogen

The total amount of nitrogen extracted from each feedstock into the aqueous phase during microwave hydrothermal processing at 120°C for 15 minutes in water alone is shown in **Figure 7-3**. The highest nitrogen (57%) was extracted from chicken manure followed by digestate (44%) and swine manure (38%). Slightly lower nitrogen was extracted from sewage sludge (32%) and microalgae (26%).

In **Figure 7-4**, the use of additives at this temperature had little effect on nitrogen extraction from swine manure. Compared to standard conditions with water (38%), slightly higher extraction was observed with NaOH and H_2SO_4 having 42% and 47% respectively. However lower extractions (23-32%) were observed while using the organic acids.

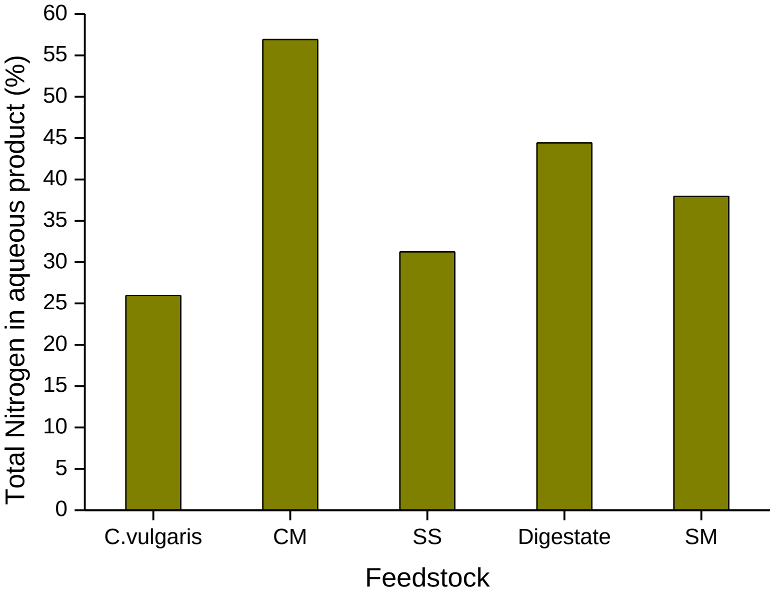
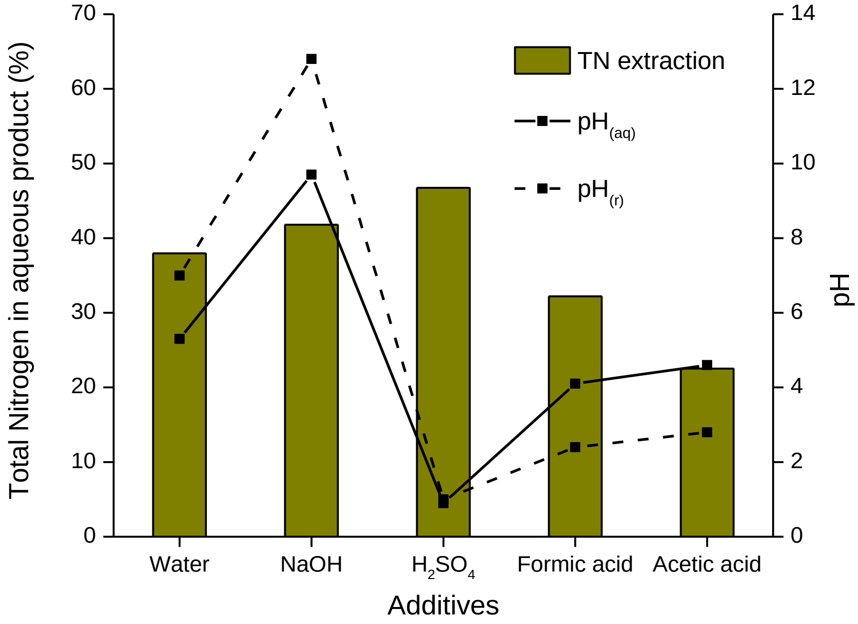


Figure 7-3: Nitrogen extraction during microwave processing of various feedstocks using de-ionised water



*$pH_{(r)}$ – pH of the starting reagent   *$pH_{(aq)}$ – pH of the recovered aqueous products

Figure 7-4: Nitrogen extraction during microwave processing of swine manure with additives

7.3.3.4 Forms of nitrogen present in the aqueous product

Figure 7-5 and **Figure 7-6** show the distribution of organic-N and NH_3-N in the aqueous product following microwave hydrothermal pre-treatment using de-ionised water and microwave pre-treatment of swine manure with various additives. Generally the aqueous products contained more organic-N than NH_3-N irrespective of the feedstock used. The levels of NH_3-N in the aqueous product from the manures were similar (25%) with similar levels of organic-N (75%). The highest NH_3-N (43%) was from sewage sludge followed by digestate (34%), and then the manures. The least ammonium was extracted from microalgae (19%). Pre-treatment of swine manure with additives slightly increased the NH_3-N which was in the range 27-31% compared to de-ionised water (25%). Again, even with the additives, the organic-N was the dominant form of nitrogen in the aqueous product in the range 69-73%. Ammonium and organic-N were both present in the aqueous product.

^{CM} Chicken manure ^{SS} Sewage sludge ^{SM} Swine manure

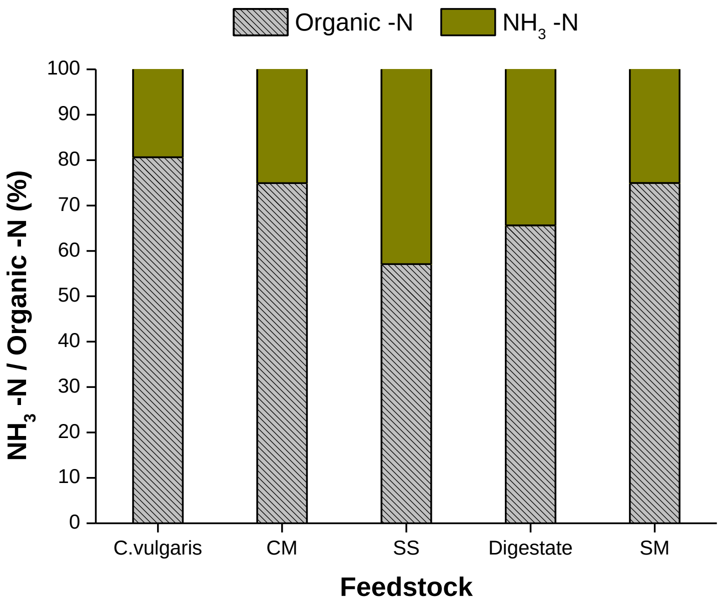


Figure 7-5: Forms of nitrogen extracted into the aqueous product during microwave processing of different feedstocks with de-ionised water

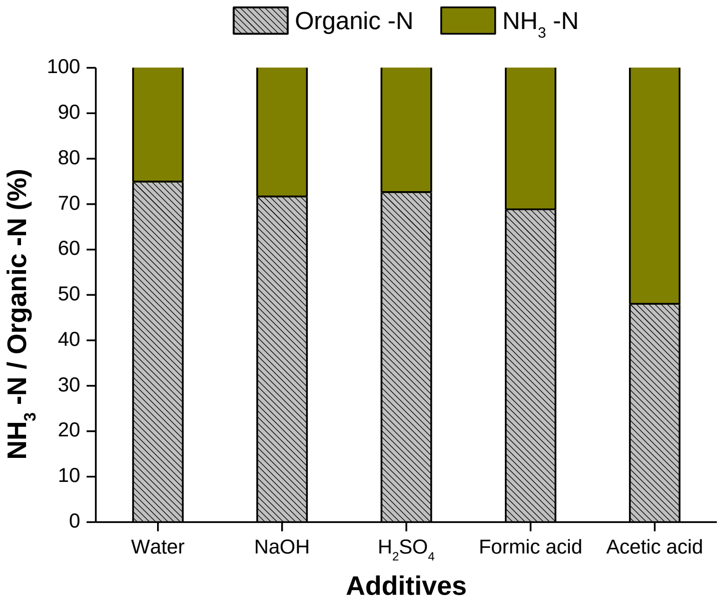


Figure 7-6: Forms of nitrogen extracted into the aqueous product during microwave processing of different feedstocks with additives

7.3.3.5 Distribution of phosphorus

The total amount of phosphorus extracted from each feedstock during microwave hydrothermal pre-treatment at 120°C for 15 minutes in water alone is shown in **Figure 7-7**. The highest level of phosphorus was extracted from chicken manure (53%) followed by microalgae (39%). Similar levels were obtained with sewage sludge and swine manure while the least was from the digestate (9%).

In **Figure 7-8**, unlike nitrogen, the use of additives at this temperature had significant effect on phosphorus extraction. Compared to the extraction with water (29%), higher extractions were observed with the acidic reagents particularly with H_2SO_4 (83%) while NaOH extracted the least phosphorus (13%).

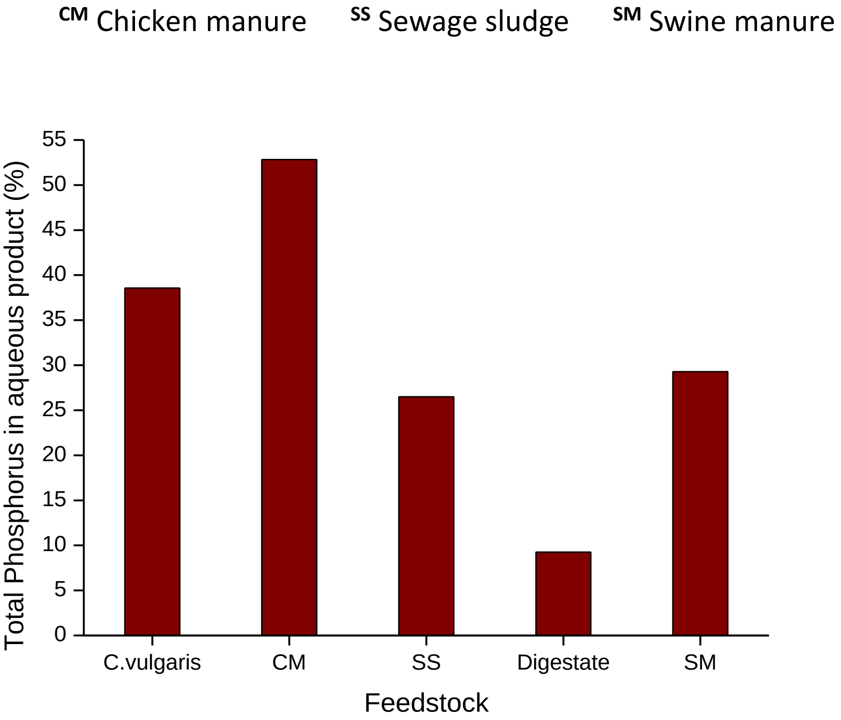
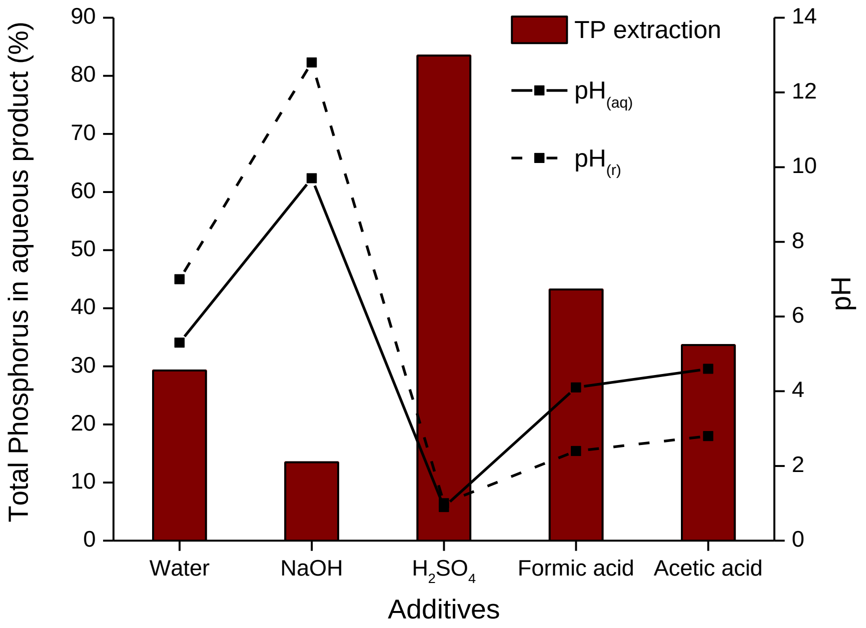


Figure 7-7: Phosphorus extraction during microwave processing of various feedstocks using de-ionised water



$^*pH_{(r)}$ – pH of the starting reagent $^*pH_{(aq)}$ – pH of the recovered aqueous products

Figure 7-8: Phosphorus extraction during microwave processing of swine manure with additives

7.3.3.6 Forms of phosphorus present in the aqueous product

Figure 7-9 show the distribution of organic-P and phosphate-P in the aqueous product following microwave pre-treatment in water. Generally the aqueous products contained both organic-P and phosphate-P. The levels of each differ with the different feedstock. Organic-P was highest with digestate while similar amount (20-27%) was observed with microalgae and chicken manure (20-27%), however the swine manure had the least (8%). With these feedstock, the dominant form of phosphorus was phosphate rather than organic-P. Both species were almost equally distributed with sewage sludge.

Figure 7-10 show the distribution of organic-P and phosphate-P in the aqueous product following microwave hydrothermal pre-treatment of swine manure with various additives. Generally phosphate was the dominant form of phosphorus in water alone and most of the additives (75-92%) while these species were almost equally distributed with the alkali. Organic-P was between 8-9% with water, H_2SO_4 and formic acid, however it was 25% with acetic acid.

^{CM} Chicken manure ^{SS} Sewage sludge ^{SM} Swine manure

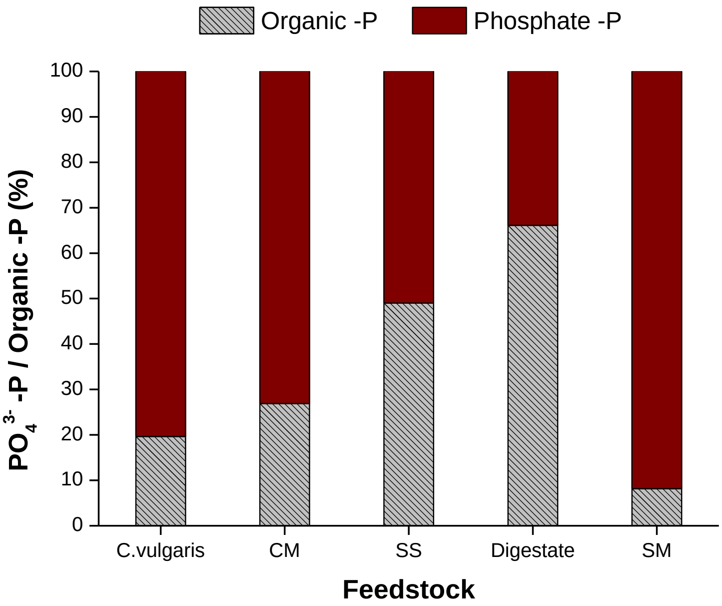


Figure 7-9: Forms of phosphorus extracted during microwave processing of different feedstocks with de-ionised water

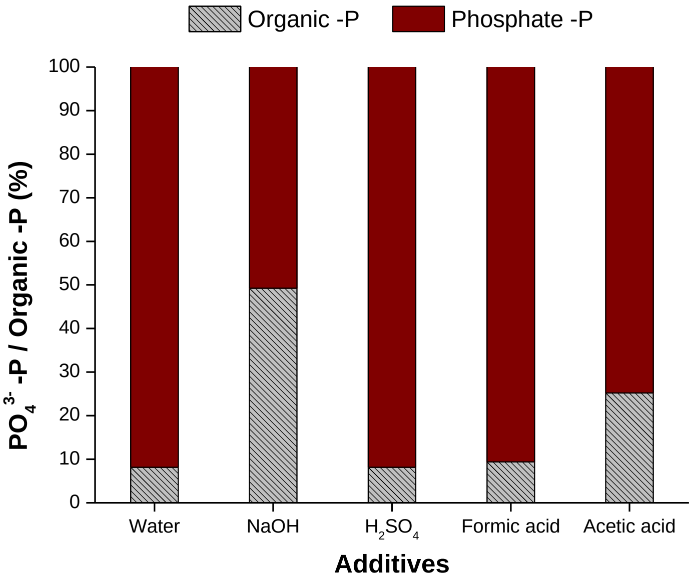


Figure 7-10: Forms of phosphorus extracted during microwave processing of different feedstocks with additives

7.3.3.7 Distribution of metals during microwave pre-treatment with water

The levels of macro elements in both the aqueous product and the solid products have been presented in **Figure 7-11** and **Figure 7-12** respectively. Although various feedstocks were pre-treated in de-ionised water using microwave heating, similar trends in the distribution of macro elements and micro elements were observed for all feedstocks. Potassium was almost completely extracted from microalgae and the manures into the aqueous product with levels more than 70% leaving the solid with very little traces of potassium. Although with sewage sludge and digestate, about 30-34% potassium was extracted with higher levels retained in the solid product. Sodium was also completely extracted into the aqueous product for all feedstock, leaving traces in the solid product as well. On the other hand, magnesium was retained more in the solid product than the aqueous product for microalgae, sewage sludge and digestate with retention between 68-85%. However with the manures, magnesium is equally distributed between both products. After pre-treatment, calcium was mainly retained in the solid product with retention levels between 77-96% for all feedstocks. Among the other feedstocks, more calcium (20%) was extracted from the sewage sludge into the aqueous product while others were between 3-7%.

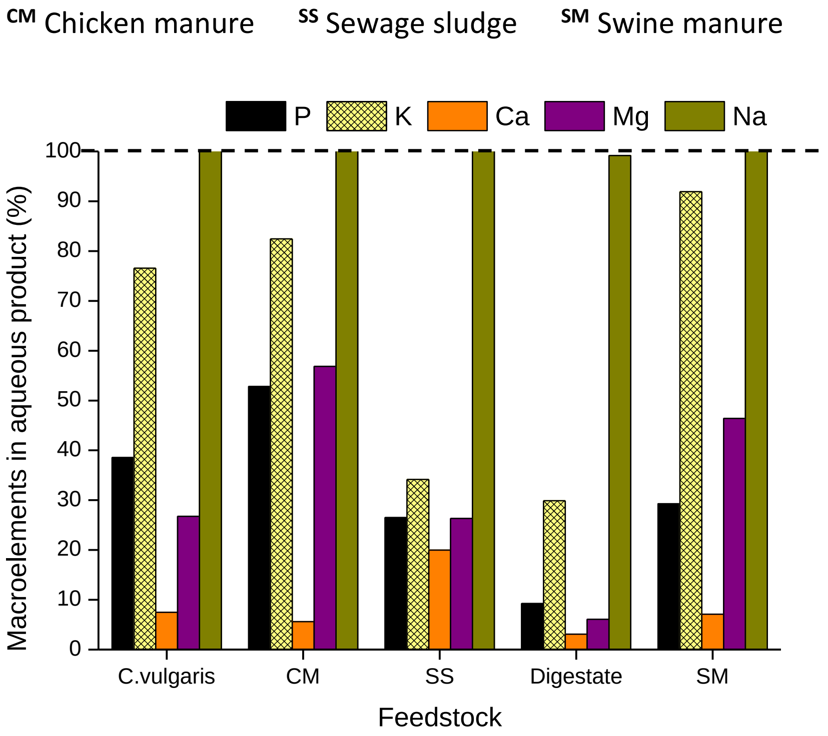


Figure 7-11: Macro elements extracted in the aqueous product during microwave pre-treatment with water

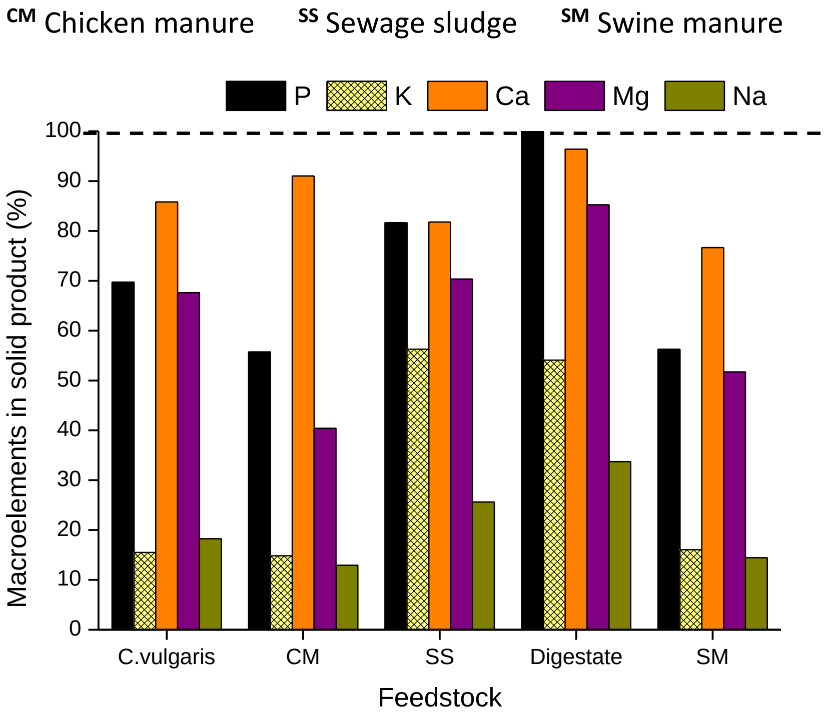


Figure 7-12: Macro elements retained in the solid product during microwave pre-treatment with water

Figure 7-13 and **Figure 7-14** show the levels of micro elements in both the aqueous product and the solid products respectively. Generally iron, cobalt, copper, manganese and zinc were mainly present in the solid product than the aqueous product with levels greater than 80%. Iron was particularly highest in the residue from sewage and digestate which is as a result of high levels of iron present in the unprocessed feedstock. There were also significant amounts of heavy metals such as lead and aluminium in the solid product with lead retention levels between 28-36% in microalgae and chicken manure while it was 72-81% for sewage sludge, digestate and swine manure. Aluminium retention levels in the solid products were more than 60% for all feedstocks.

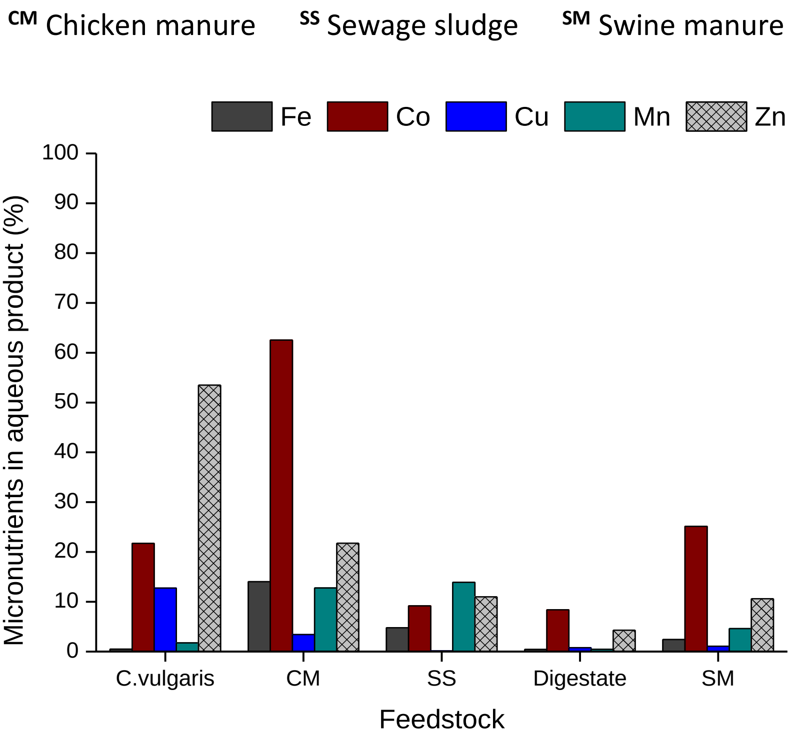


Figure 7-13: Micro elements extracted in the aqueous product during microwave pre-treatment with water

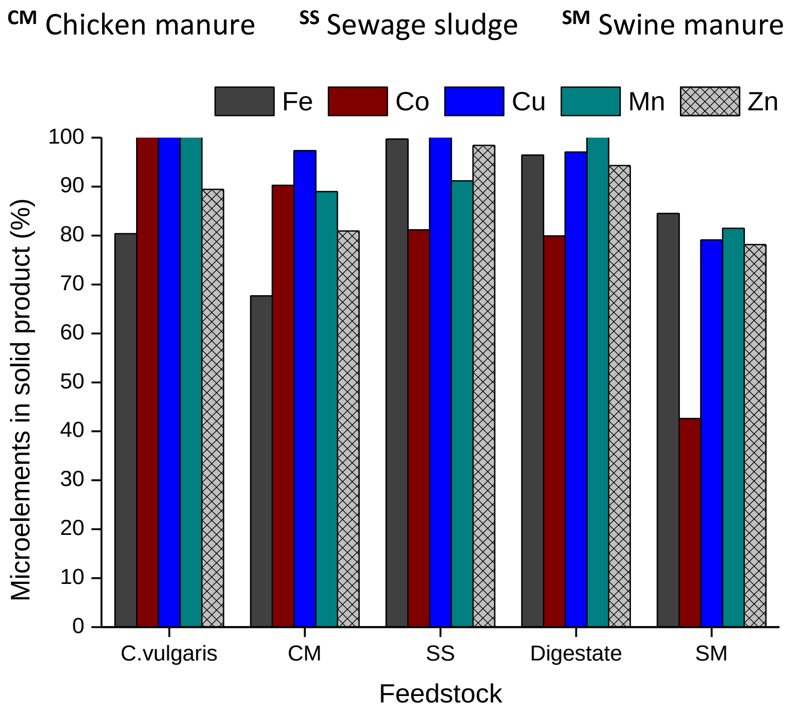


Figure 7-14: Micro elements retained in the solid product during microwave pre-treatment with water

7.3.3.8 Distribution of metals during microwave pre-treatment with additives

Swine manure was pre-treated with various additives-alkali, mineral acid and organic acids using microwave heating at 120°C for 15 minutes. **Figure 7-15** and **Figure 7-16** show the levels of macro elements in both the aqueous products and solid products recovered after pre-treatment with these additives. It was observed that the use of additives had significant effect on the distribution of macro elements between the aqueous and the solid products. The acidic reagents, especially H_2SO_4, extracted the most macro elements followed by formic acid and lastly acetic acid. Compared to the acidic reagents, neutral and alkali conditions favoured more retention of macro elements such as phosphorus, calcium and magnesium in the solid product than the aqueous product. Extraction of calcium was between 1-7% under neutral and alkali conditions whereas it was 25-37% using the organic acid and even higher (51%) using H_2SO_4. Potassium and sodium, like pre-treatment with de-ionised water, were almost completely extracted into the aqueous product using these additives.

As discussed earlier in the previous section, higher extraction of phosphorus was achieved under acidic conditions than under neutral or alkaline conditions. Under neutral and alkaline conditions, higher amounts of calcium (77-89%) were retained in the solid product than in the aqueous product while lower amounts of calcium was retained in the solid after using the acidic reagents; H_2SO_4 (34%), formic acid (47%) and acetic acid (67%). Under normal conditions with water, magnesium was equally distributed between the two products. However with NaOH, higher magnesium was retained in the solid than in the aqueous product which was about 4%. Generally with the acidic reagents, lower magnesium is retained in the solid as most of it is extracted into the aqueous product.

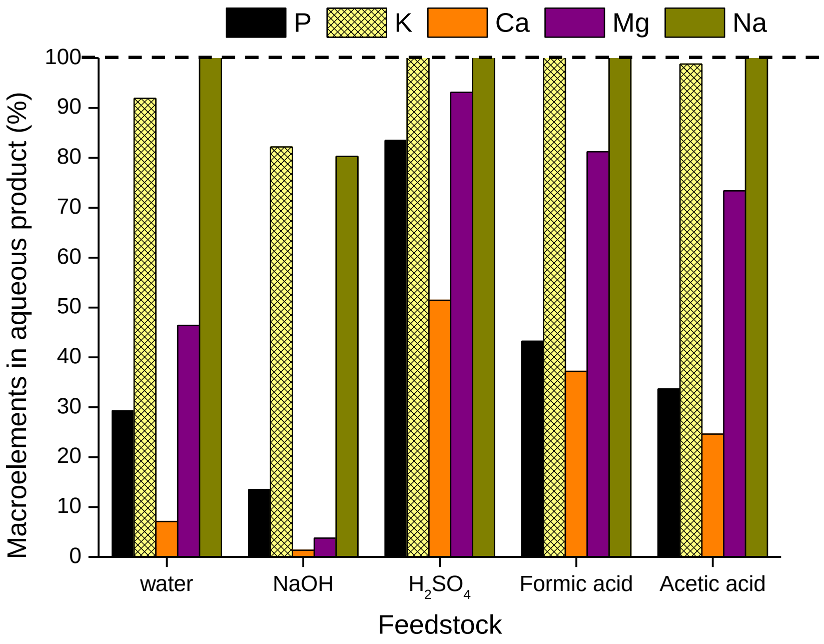


Figure 7-15: Macro elements extracted in the aqueous product during microwave pre-treatment with additives

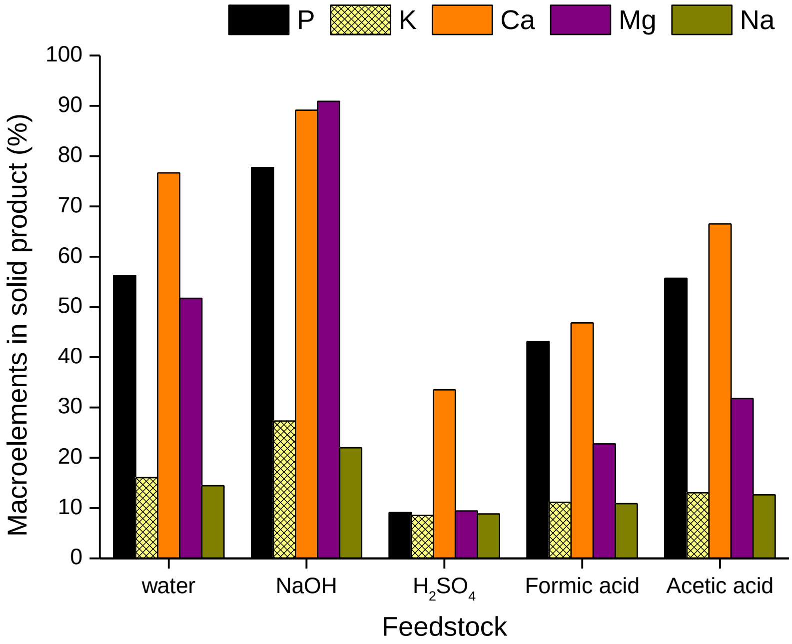


Figure 7-16: Macro elements retained in the solid product during microwave pre-treatment with additives

Figure 7-17 and **Figure 7-18** show the levels of micro elements in both the aqueous and solid products recovered after pre-treatment with additives. The additives had significant effect on the extraction of these elements into the aqueous product. Most of the microelements were retained in the solid product after pre-treatment with water, NaOH and organic acids. However higher extraction of iron, cobalt, manganese and zinc were observed with H_2SO_4. Extraction of manganese and zinc were between 83-87% while iron and cobalt were 60-66%. Significant quantities of cobalt, manganese and zinc were extracted with the organic acids however they were much lesser than the amounts extracted with H_2SO_4. Formic acid extracted between 41-43% manganese and zinc as well as 30% cobalt. Whereas similar quantities 27-28% of these elements were extracted with acetic acid. The residues with H_2SO_4 had less than 13% manganese and zinc, about 23-34% iron and cobalt and about 68% copper.

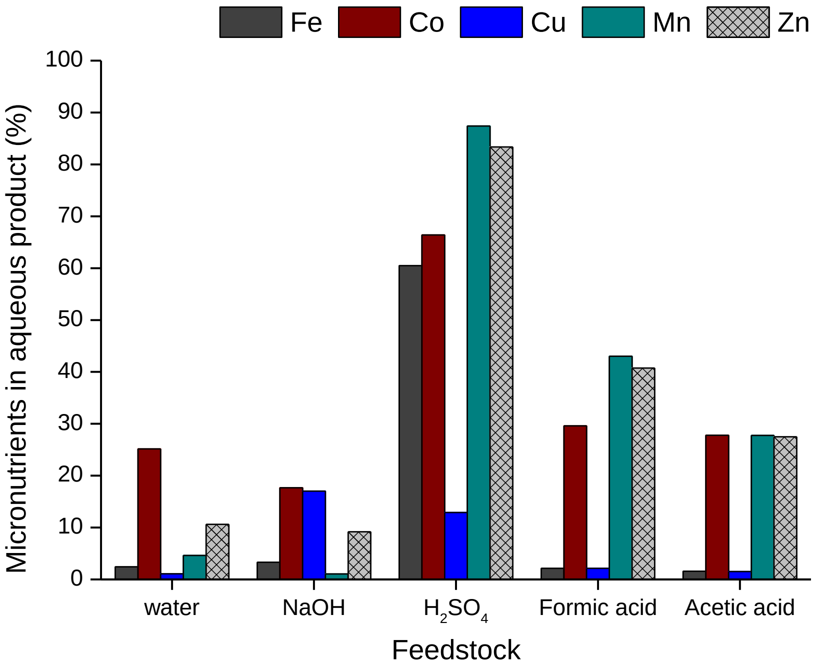


Figure 7-17: Micro elements extracted in the aqueous product during microwave pre-treatment with additives

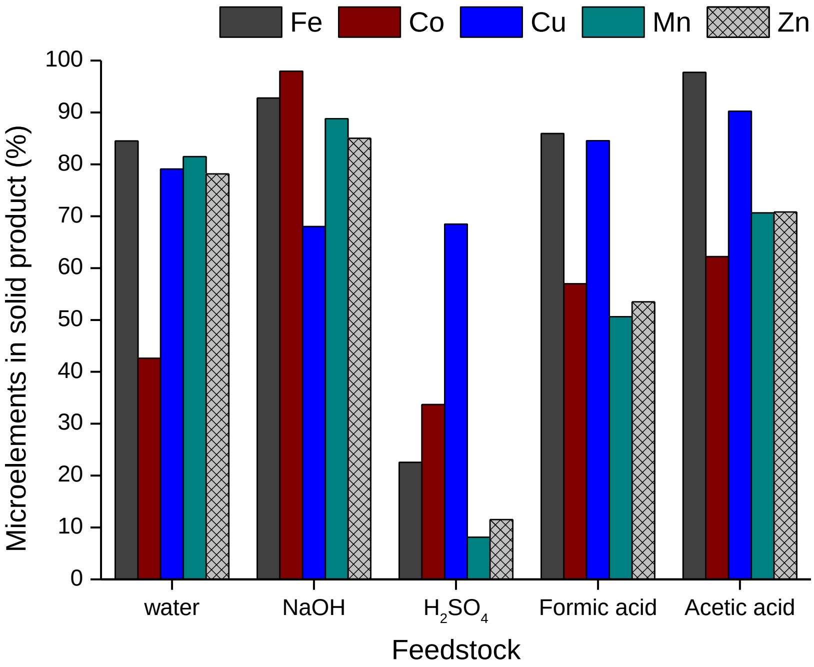


Figure 7-18: Micro elements retained in the solid product during microwave pre-treatment with additives

7.4 Comparing nutrient extraction using microwave heating and conventional heating using additives

Pre-treatment of swine manure with different reagents such as alkali – 0.1M sodium hydroxide, mineral acid- 0.1M sulphuric acid and the organic acids, 0.1M acetic acid and 0.1M formic acid were performed using the microwave heating and the conventional heating. Although pre-treatment of this feedstock was at similar temperature (120°C), the residence time was shorter (15 minutes) for the microwave heating while it was longer (60 minutes) for the conventional heating.

Figure 7-19 shows the nitrogen extracted using both heating approaches and the different reagents. Under normal conditions with de-ionised water, there was 9% increase in nitrogen extraction using the microwave heating. Also, higher nitrogen extraction between 13-19% was achieved with NaOH and H_2SO_4 while it was only 5% with formic acid. There was no significant change in nitrogen extraction using acetic acid.

Unlike nitrogen, as shown in **Figure 7-20**, microwave heating slightly increased the amount of phosphorus extracted using the various reagents compared to conventional heating. Phosphorus extraction increased between 2-4% with NaOH and H_2SO_4, 7% with acetic acid but significantly higher (17%) with formic acid. However the type of heating did not affect the levels of phosphorus extracted using de-ionised water.

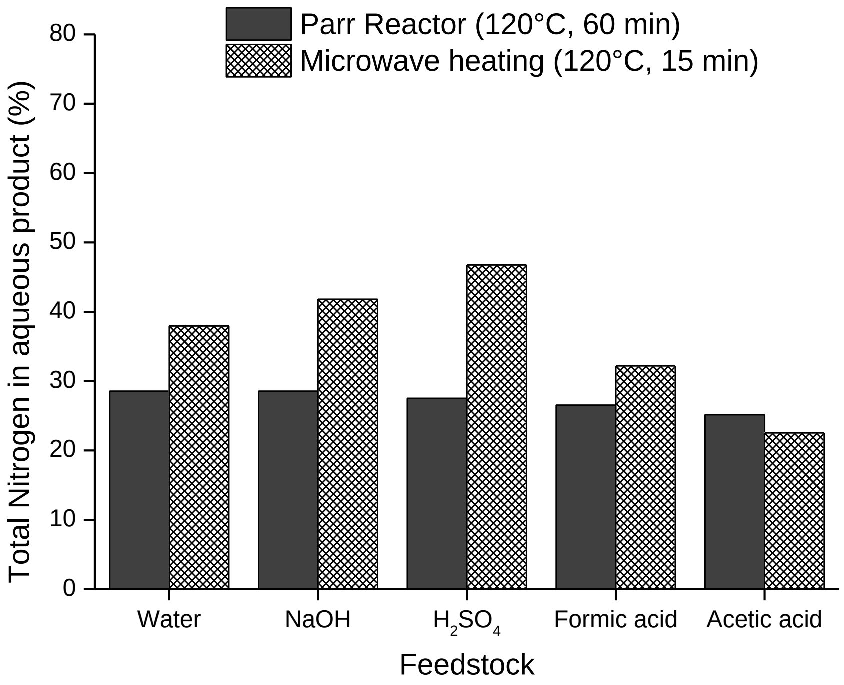


Figure 7-19: Nitrogen extraction during microwave heating and hydrothermal heating of swine manure using additives

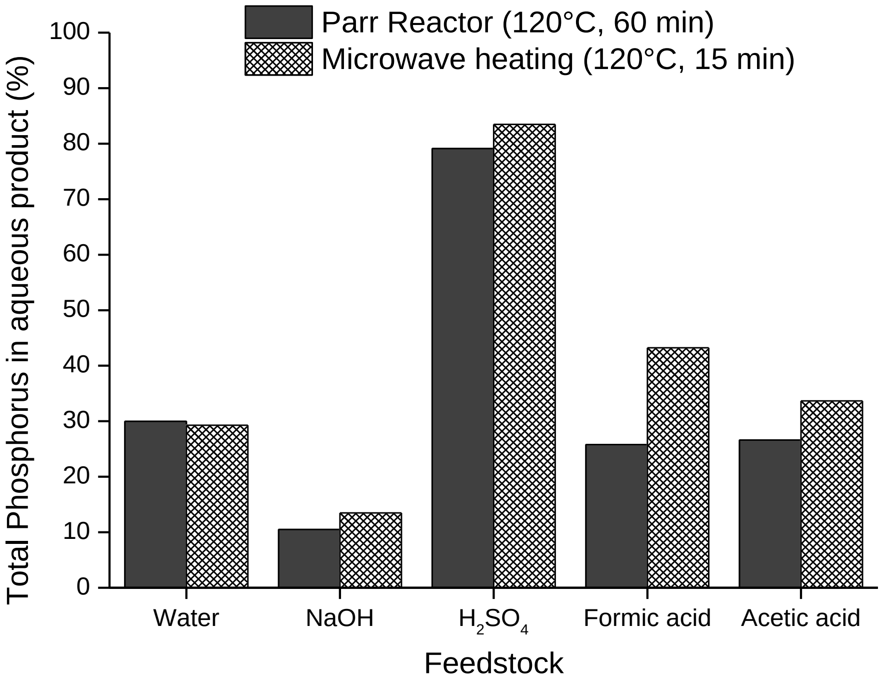


Figure 7-20: Phosphorus extraction during microwave heating and hydrothermal heating of swine manure using additives

7.5 Conclusion

Microwave heating was employed as a pre-treatment method for various biomass under normal conditions with water and with additives for only swine manure. The levels of nutrients extracted under these conditions was investigated. Also the influence of these conditions on metal extraction into the aqueous products and retention in the solid product was also investigated. The results show that aqueous product recovered after microwave pre-treatment under normal conditions with water contain significant levels of nitrogen and phosphorus. Nitrogen was mainly in the form organic-N for most feedstocks while phosphorus in the aqueous product was mainly in the form of organic-P with sewage sludge and digestate, but occurred mainly as phosphate with microalgae, and manure. Also with most additives, the aqueous product was mainly in the form of organic-N than NH_3-N except for acetic acid which had equal levels of these forms of nitrogen. Higher TN extraction was achieved with water, alkali and mineral acid rather than the organic acids while higher TP extraction was achieved with the acidic reagents rather than water or NaOH. With most additives, phosphorus was present in the aqueous product as phosphate rather than organic-P except with NaOH which had equal distribution of these forms.

Aqueous products from microwave pre-treatment contain most of the potassium and sodium present in the unprocessed feedstock. Higher potassium was extracted with microalgae and manures but not with sewage sludge and digestate. The microwave residues contain mainly calcium, magnesium and phosphorus for most feedstocks. Under normal conditions with water, microelements are mostly concentrated in the residue than the aqueous product. Acidic conditions favour extraction of macro elements such as Ca, Mg, P and micro elements such as Co, Mn and Zn unlike neutral or alkaline conditions which extracted less of these elements making them concentrated in their residues. In particular with H_2SO_4, the highest levels of Fe, Co, Mn and Zn were extracted.

In comparison with microwave heating and conventional heating in terms of extracted nutrient levels, conventional heating favour TN extraction from microalgae, digestate and chicken manure. Both heating methods do not affect TP extraction from microalgae and digestate, however with manures, microwave heating has the potential to extract more TP from these feedstocks. Pre-treatment of feedstocks using microwave heating at low temperature (120°C) and shorter retention time (15 minutes) favour TN extraction with H_2SO_4, NaOH and water than with the organic acids when compared with conventional heating at the same temperature for 60 minutes. Also microwave heating increased TP extraction especially with the acidic reagents compared to conventional heating.

Chapter 8 Recovery of nutrients from hydrothermal aqueous waste streams

8.1 Introduction

This study aim is to investigate the potential of utilising hydrothermal aqueous waste streams for nutrient recycling either by biological recovery using microalgae or physical recovery of phosphorus by adsorption on a Mg-treated biochar derived from oak.

8.2 Biological nutrient recovery

Biological recovery of nutrients from various hydrothermal aqueous products involved several cultivation trials with fresh water microalgae- *Chlorella vulgaris*. These trials were performed in batches to determine the maximum biomass concentration and the most suitable dilution factor required to enhance its growth. Aqueous products from high temperature processing – supercritical water gasification (SCWG) were used as previous studies in this research have shown that these aqueous products contain most of the nitrogen initially present in the feedstock. In order to establish a closed hydrothermal processing loop with integrated nutrient recycling for algae cultivation, these aqueous products were utilized. Algal biomass obtained by this means could be used as starting material in the algal refinery.

The SCWG aqueous products used as culture media were diluted to 1:50, 1:200 and 1:400. These dilutions were chosen as lower dilution of aqueous product from HTL *Spirulina* i.e. 1:10 was reported as being too strong, having inhibitory effects with no microalgal growth observed (Umakanta Jena et al., 2011b). Also SCWG aqueous products contain more inhibitory species compared to HTL of the same feedstock.

8.2.1 Using aqueous product from catalysed and non- catalysed SCWG

8.2.1.1 Characterisation of aqueous product

Super-critical water gasification (SCWG) of seaweeds – *Saccharina* and *Alaria esculenta* were conducted using the reactor and operating conditions described in **Chapter 3**.

Two SCWG experiments were conducted for each seaweed, one using heterogeneous catalyst 5% Ru/Al_2O_3 (Ruthenium Alumina catalyst) denoted by '**C**' while in the other denoted by '**NC**', no catalyst was added. The experiment was conducted to determine the effect of catalyst addition on the gas yields obtained via SCWG. The results on gas yields are not presented as it is beyond the scope of this objective. Cultivation trials were only performed to evaluate the potential of utilizing the nutrients in these waste streams. For the purpose of this work, only the composition of the aqueous product and its effect on biomass concentration was investigated. The aqueous products were recovered and extensively characterized to determine the relative quantities of total organic carbon (TOC), total nitrogen (TN), ammonium (NH_4^+), phosphate (PO_4^{3-}), potassium (K^+), acetate, nitrate (NO_3^-) and phenols present using the separation technique and analytical techniques detailed in **Chapter 3**. These aqueous products were the used as culture media to grow *Chlorella vulgaris* at different dilution ratios while the Bold's Basal media (BBM) was used as the control experiment. The quantities of these analytes in the aqueous products and standard BBM media are presented in **Table 8-1**.

Table 8-1: Characterisation of aqueous products from SCWG of *Saccharina latissima* and *Alaria esculenta*

	Concentration (mg/L)				
Species	*S.latissima* NC	*S.latissima* C	*A.esculenta* NC	*A.esculenta* C	BBM
TOC	4,310	3,290	3,710	2,360	-
TN	910	1,270	1,120	2,060	40
NH_4^+	700	1,180	620	1,040	-
PO_4^{3-}	n/d	20	n/d	n/d	150
K^+	5,720	4,660	1,720	1,820	80
Acetate	1,470	1,230	n/d	n/d	-
NO_3^-	170	480	300	180	180
Phenols	410	150	480	70	-

$^{n/d}$ Not determined
^{NC} Non-catalysed
^{C} Catalysed

The concentration of species in the aqueous products recovered from SCWG of *S.latissima* and *A.esculenta* with catalyst (**C**) and without catalyst (**NC**) varied. However similar trends were observed for both seaweeds. The use of catalyst reduced the concentration of total organic carbon (TOC) in the aqueous products. On the other hand, catalysed SCWG increased the concentration of both the total nitrogen (TN) and ammonium to 1,270 mg/L and 1,180 mg/L respectively for *S.latissima* whereas it was 2,060 mg/L and 1,040 mg/L respectively for *A.esculenta*. For non-catalysed SCWG, ammonium was between 620-700 mg/L while TN was between 910-1,120 mg/L. The levels of potassium in the aqueous products was fairly constant for both the catalysed and non-catalysed SCWG conditions. Acetate was slightly lower using catalyst. Also phenol concentration reduced with the addition of catalyst for both seaweeds. For instance phenol in the non-catalysed SCWG of *S.latissima* was 410 mg/L which reduced significantly to 150 mg/L with catalyst.

8.2.1.2 Cultivation Trials

Due to time constraints, cultivation trials were only performed using different dilutions (1:50, 1:200 and 1:400) of both the catalysed and non-catalysed SCWG aqueous products from *S.latissima* in separate 500mL bioreactors. Each bioreactor contained 200mL of the culture media either the diluted aqueous products or the standard Bold's Basal media (BBM). Each flask was inoculated with stock culture of *C.vulgaris* which was growing at exponential phase in the vertical bioreactors (shown in **Figure 3-7**). On a daily basis, turbidity and pH measurements of the growing cultures in **Figure 8-1** were taken over the 14-day cultivation period.

Table 8-2: Concentration of nutrients in the culture media from SCWG of *Saccharina latissima* after dilution

	Concentration (mg/L)				
Culture media	TN	NH_4^+	PO_4^{3-}	K^+	NO_3^-
BBM	40	-	150	80	180
C 1:50	25.4	23.6	0.4	93.2	9.6
C 1:200	6.35	5.9	0.1	23.3	2.4
C 1:400	3.18	2.95	0.05	11.65	1.2
NC 1:50	18.2	14	n/d	114.4	3.4
NC 1:200	4.55	3.5	n/d	28.6	0.85
NC 1:400	2.28	1.75	n/d	14.3	0.43

$^{n/d}$ Not determined

Figure 8-1: *C.vulgaris* growing in diluted catalysed and non-catalysed SCWG aqueous products

8.2.1.3 Growth Kinetics

Data from both the turbidity and pH measurements of the different cultures over a 14-day cultivation period are shown in **Tables 6** and **Table 7** in **Appendix 3**. Cumulative growth curves for the cultures growing in the non-catalysed aqueous products and the catalysed aqueous products are shown in **Figure 8-2** and **Figure 8-3** in order to compare the growth rates of *C.vulgaris* in the various culture media investigated. The growth curve is a function of log turbidity. These graphs show that the standard Bold's media had the most biomass compared to either the catalysed or non-catalysed aqueous products. Generally for the two types of aqueous products, higher growth was observed in the lower dilution- 1:50 compared to the other dilutions investigated. This may be attributed to the limiting nutrients with higher dilution causing a decreased growth rate in the cultures. During the exponential growth phase as shown in **Table 8-3**, the specific growth rates in the catalysed aqueous products was slightly higher than the specific growth rates obtained in the non-catalysed aqueous products. This is most likely attributed to the presence of higher nutrients especially nitrogen in the catalysed SCWG aqueous product after dilution as shown in **Table 8-2**.

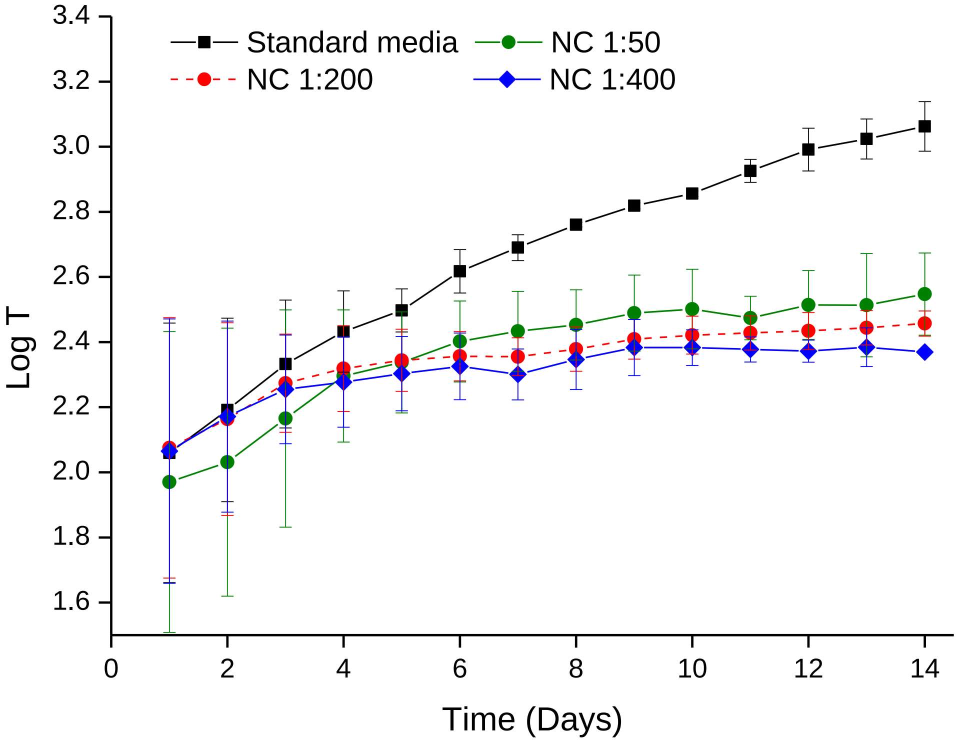


Figure 8-2: Growth of *C.vulgaris* in aqueous products from non-catalysed SCWG of *S.latissima*

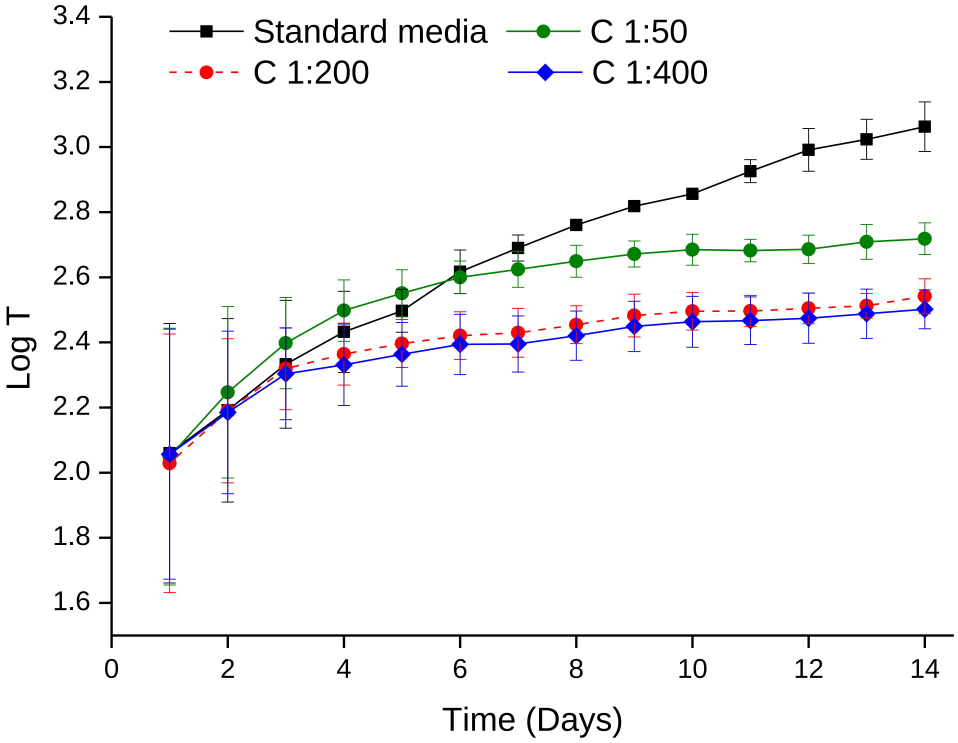


Figure 8-3: Growth of *C.vulgaris* in aqueous products from catalysed SCWG of *S.latissima*

Individual growth curves with a corresponding pH change in each bioreactor over the cultivation period have been shown in **Figure 8-4** to **Figure 8-10**. Generally, the growth curves for cultures in the various dilutions using catalysed SCWG aqueous product started with a noticeable and significant exponential phase which is similar to the culture growing in the standard media. However there was a little lag period for the 1:50 aqueous product without catalyst. In the bioreactors having 1:200 and 1:400 dilution of aqueous product without catalyst, there was no noticeable lag period as the culture proceeded to the exponential phase just as the culture growing in the standard media.

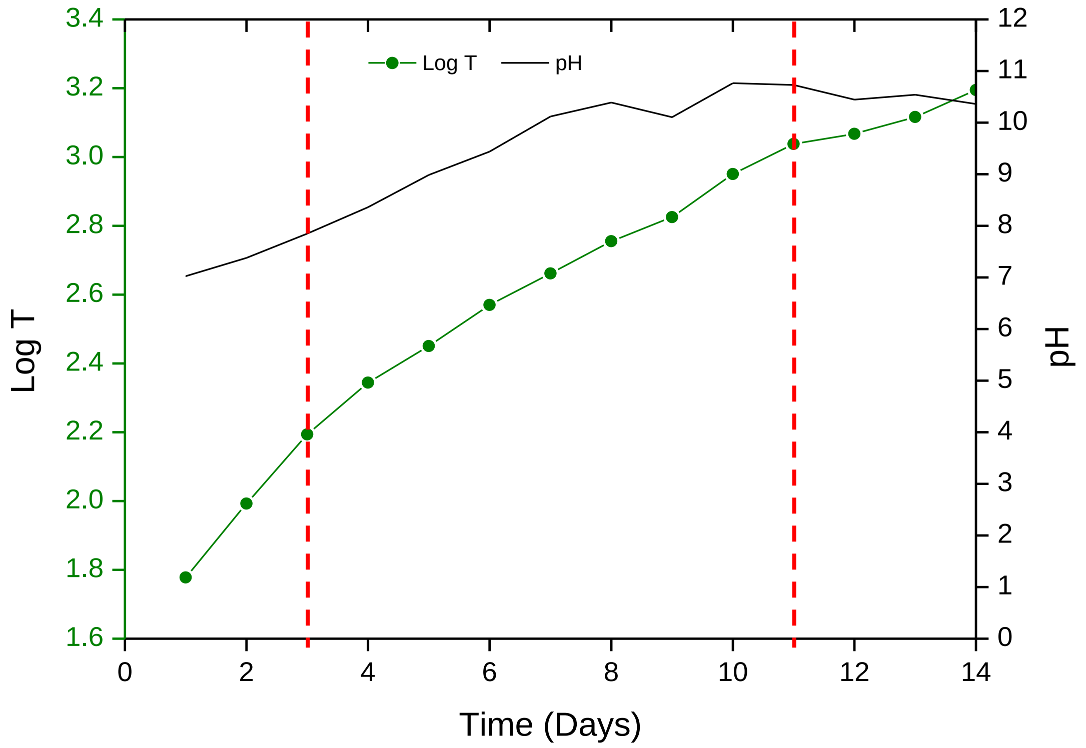


Figure 8-4: Growth Phases and pH change in Standard Bold's Basal Medium

Figure 8-4 shows the growth curve of *C.vulgaris* in the standard Basal Bold media (BBM) which was used as the control experiment. The growth curve shows that *C.vulgaris* did not undergo a lag phase as it exhibited rapid growth within the first 3 days having specific growth rate of 0.21day^{-1}. The absence of the lag phase on the growth curve is likely due to *C.vulgaris* adapting to the standard media while growing as a stock culture for inoculation using the vertical bioreactor. However, between day 3 and day 11, its specific growth rate reduced to 0.11day^{-1} which further reduced to a much lower specific growth rate of 0.05day^{-1} between day 13 and day 14. The culture did not completely reach stationary phase before the end of the cultivation period. The pH of the culture media increased significantly from 6.61 to 10.11 throughout the 14-day period.

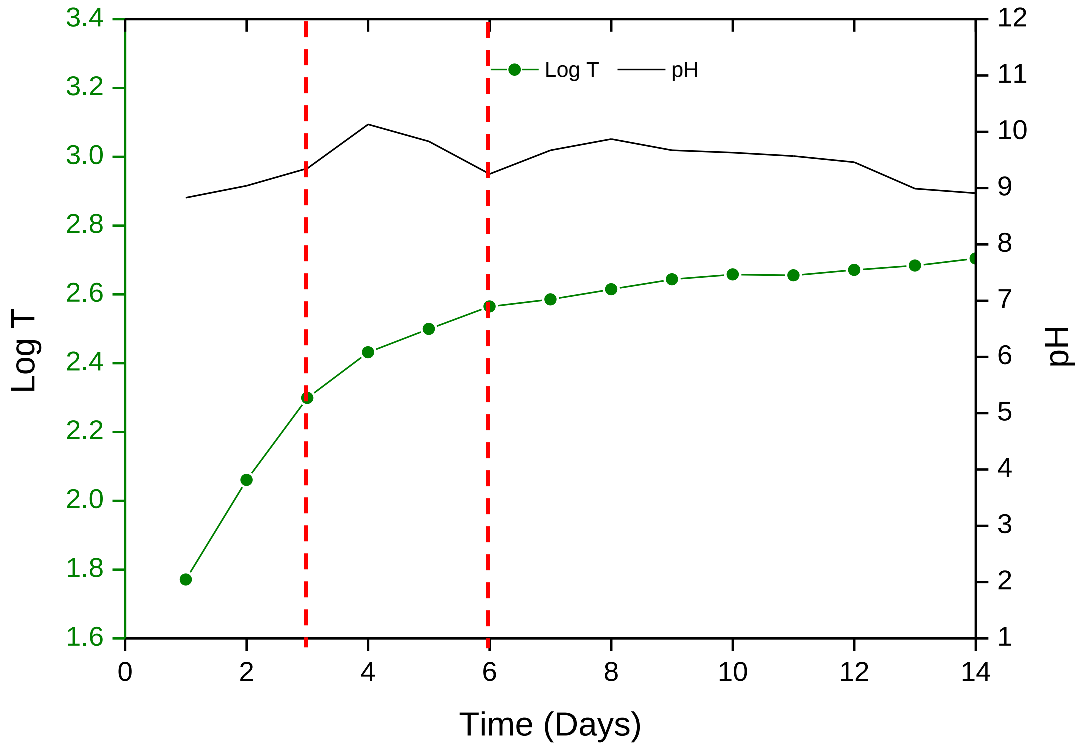


Figure 8-5: Growth phases and pH change in catalysed SCWG aqueous product 1:50

Figure 8-5 shows the growth curve of *C.vulgaris* in aqueous product from catalysed SCWG diluted at 1:50. The culture did not show any lag phase after inoculation, instead it proceeded to the exponential phase with specific growth rate of 0.26day^{-1}. The culture exhibited rapid growth within the first 3 days, which lasted until day 6 when it gradually approached the stationary phase. Its specific growth rate at the start of stationary phase was 0.07 day^{-1} which further reduced to 0.02 day^{-1} at the end of the cultivation period. The pH of the culture medium changed significantly from 8.83 to 10.13 during the rapid growth period within 4 days. However the pH dropped sharply to 9.25 by day 6 which corresponds to the beginning of its stationary growth phase. The pH increased slightly to 9.87 by day 8 and reduced gradually afterwards until the end of cultivation. At this time, the culture had attained a consistent stationary phase.

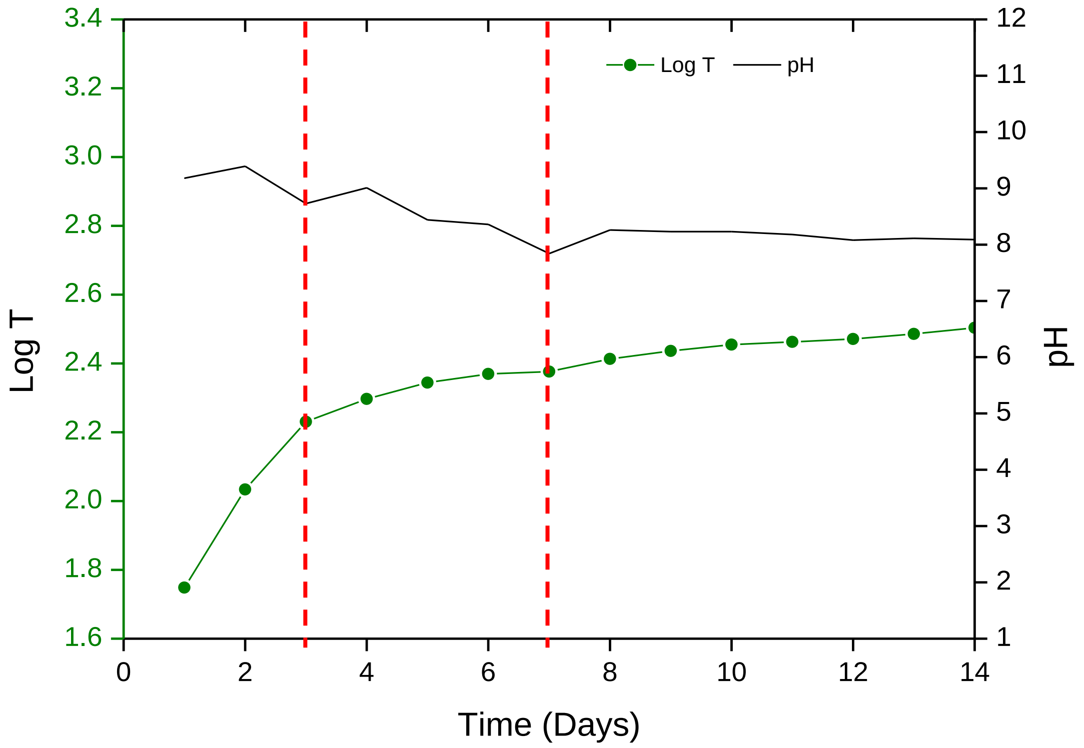


Figure 8-6: Growth Phases and pH change in catalysed SCWG aqueous product 1:200

Figure 8-6 shows the growth of *C.vulgaris* in aqueous product from catalysed SCWG diluted at 1:200. Again there was no lag phase instead it adapted well to the culture medium, growing exponentially at 0.24 day^{-1} within the first 3 days. After this time, there was no more rapid growth, instead the growth rate gradually reduced to 0.03 day^{-1} at the start of the stationary phase until day 7 and further reduced to 0.02 day^{-1} at the end of the cultivation period. Its growth rate reduced significantly after this time and approaching the stationary phase. During the growth period, the pH of the culture changed from 9.18 to 7.84 at day 7 after which it was fairly constant until the end of cultivation period.

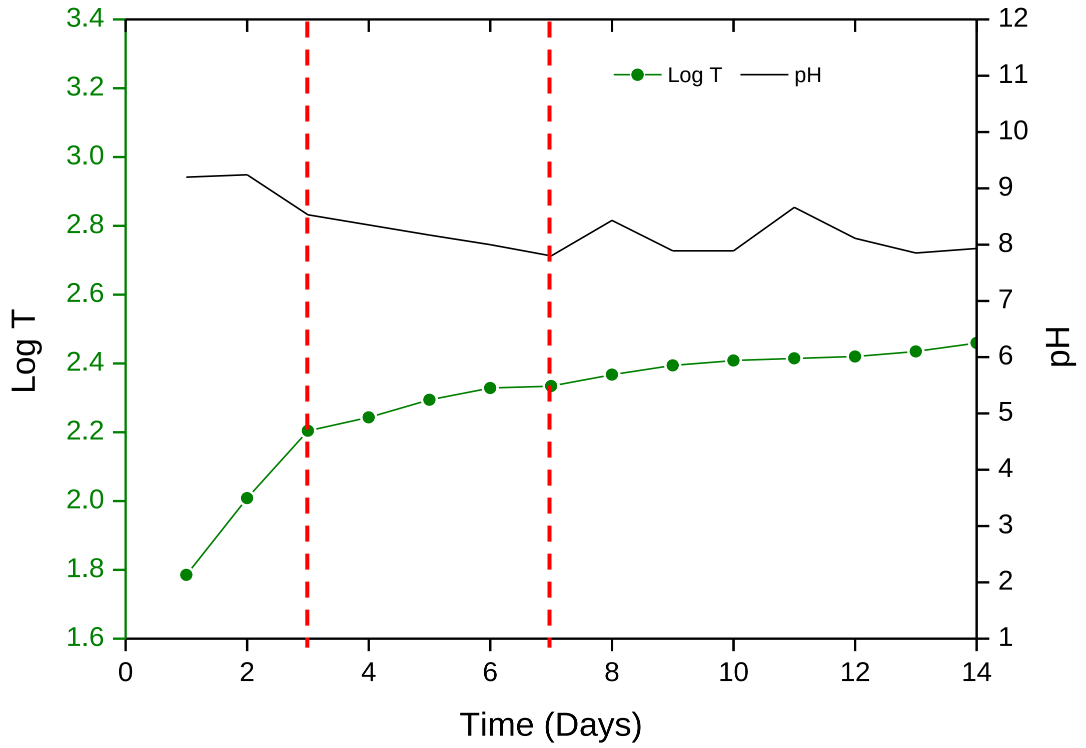


Figure 8-7: Growth Phases and pH change in catalysed SCWG aqueous product 1:400

Figure 8-7 shows the growth of *C.vulgaris* in aqueous product from catalysed SCWG diluted at 1:400. There was also no lag phase and growth was exponential in the first 3 days growing at 0.21 day^{-1} after which the growth rate gradually decreased to 0.03 day^{-1} when it approached stationary phase at day 7. Throughout the growth period, the pH reduced significantly from 9.2 to 7.8 and was fairly constant after this period corresponding to the beginning of stationary phase.

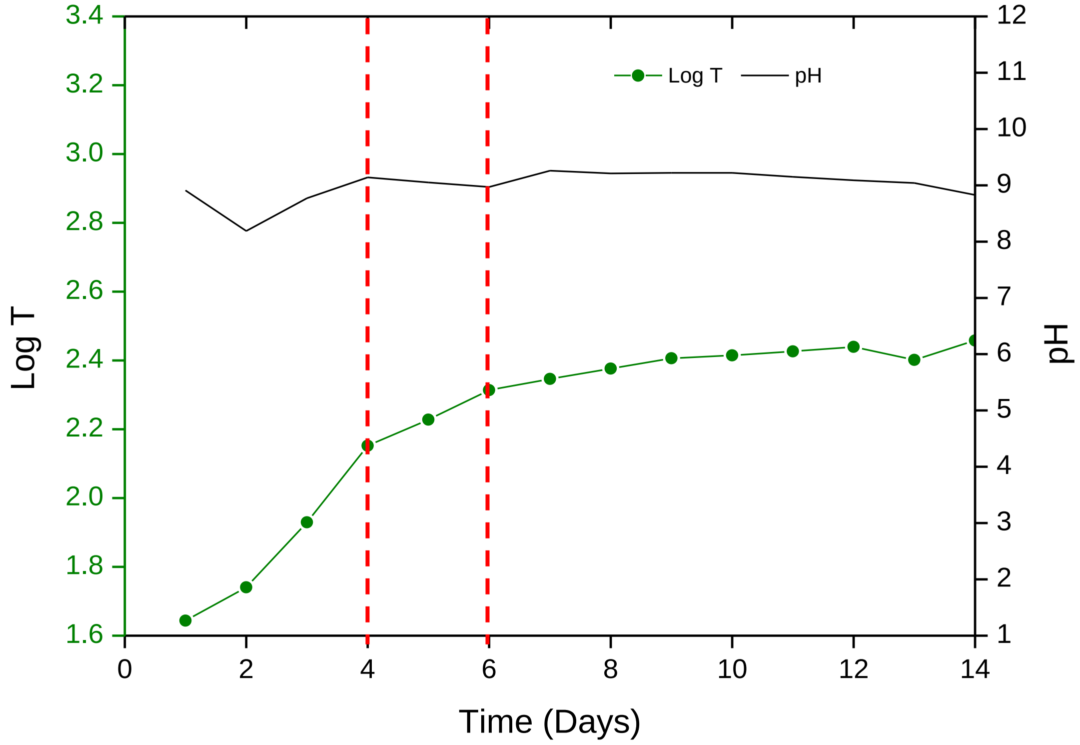


Figure 8-8: Growth Phases and pH change in non-catalysed SCWG aqueous product 1:50

Figure 8-8 shows the growth of *C.vulgaris* in aqueous product from non-catalysed SCWG diluted at 1:50. It shows that there was a two day lag period with culture growing at 0.1 day^{-1}. Its specific growth rate doubled between day 2 and day 4 but reduced to 0.08 day^{-1} between day 4 and day 6 which was the start of the stationary phase. Beyond this point, its growth rate further reduced to 0.03 day^{-1} and by the end of the cultivation period, its growth rate was 0.01 day^{-1}.

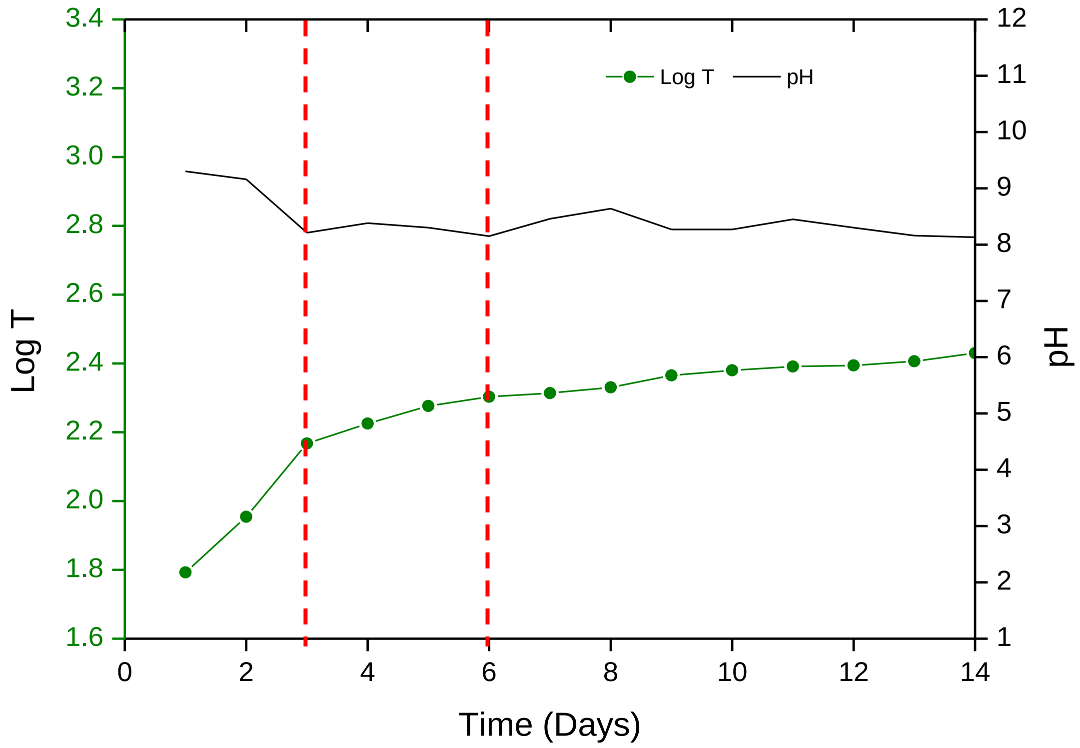


Figure 8-9: Growth Phases and pH change in non-catalysed SCWG aqueous product 1:200

Figure 8-9 shows the growth of *C.vulgaris* in aqueous product from non-catalysed SCWG diluted at 1:200. Unlike the culture growing in NC 1:50 (**Figure 8-8**), this culture did not undergo a lag phase. The culture exhibited an exponential growth rate of 0.19 day^{-1} until day 3 which reduced to 0.05 day^{-1} afterwards when it began approaching stationary phase at day 6. During the exponential phase, the pH significantly changed from 9.3 to 8.15 while the pH was fairly constant during the stationary phase until the end of cultivation at day 14.

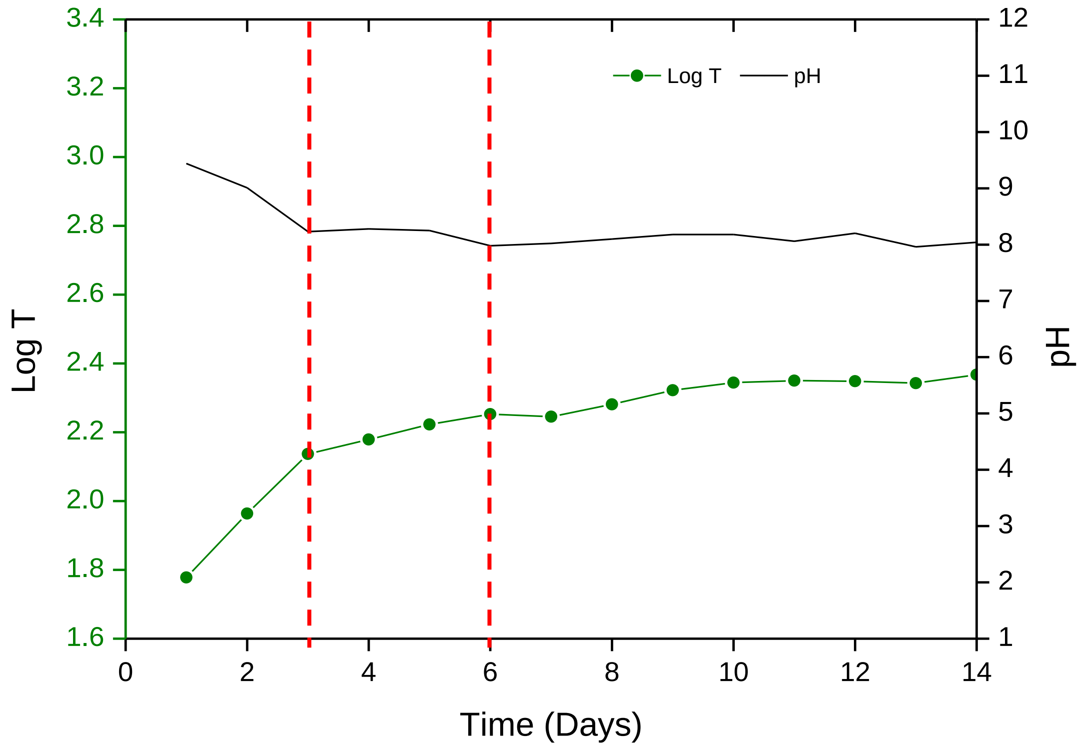


Figure 8-10: Growth Phases and pH change in non-catalysed SCWG aqueous product 1:400

Figure 8-10 shows the growth of *C.vulgaris* in aqueous product from non-catalysed SCWG diluted at 1:400. There was no noticeable lag phase however the culture grew exponentially for the first 3 days at a specific growth rate of 0.18 day^{-1} with a corresponding change in pH from 9.44 to 8.23. Afterwards, the growth rate reduced significantly to 0.04 day^{-1} until day 6 when it approached the stationary phase. During this period the pH reduced further to 7.98 and remained fairly constant during the stationary phase until the end of the cultivation period.

Table 8-3: Summary of *C.vulgaris* specific growth rate in various catalysed and non-catalysed SCWG aqueous products

	Specific Growth Rate (day^{-1})				
Culture Media	Lag Phase	Early Exponential phase	Later Exponential phase	Early Stationary phase	Later Stationary phase
Standard BBM	*	0.21	0.11	0.05	0.05
Saccharina C 1:50	*	0.26	0.07	0.02	0.02
Saccharina C 1:200	*	0.24	0.03	0.02	0.02
Saccharina C 1:400	*	0.21	0.03	0.02	0.02
Saccharina NC 1:50	0.10	0.21	0.08	0.03	0.01
Saccharina NC 1:200	*	0.19	0.05	0.02	0.02
Saccharina NC 1:400	*	0.18	0.04	0.03	0.02

*No lag phase

Table 8-3 summarizes the individual growth rates during the lag, exponential and stationary phases for *C.vulgaris* culture growing in the various bioreactors (**Figure 8-4** to **Figure 8-10**). In the standard Bold's Basal medium, *C.vulgaris* maintained exponential growth at the start of cultivation until day 11 when its growth rate reduced as it approached stationary phase. However compared to growth in this standard medium, *C.vulgaris* exhibited exponential growth during the first 3 days in the diluted catalysed SCWG culture media and only 2 days in the diluted non-catalysed SCWG culture media. For both the catalysed and non-catalysed aqueous products, the exponential growth rate of *C.vulgaris* in 1:50 dilution was highest followed by growth rate in 1:200 and lastly 1:400 which is most likely attributed to nutrient limitation in these bioreactors as indicated by the decreasing nutrient composition with an increase in dilution factor (**Table 8-2**). The longer exponential growth period observed in the culture growing in the standard Bold's Basal medium is as a result of sufficient nutrients present in the culture media. In the standard medium, the starting concentration of TN, PO_4^{3-}, NO_3^- was 40mg/L, 150mg/L and 180mg/L respectively whereas TN in the least diluted culture medium -NC 1:50 and C 1:50 was about 18 mg/L and 25 mg/L respectively. Ammonium is the main form of nitrogen present in SCWG aqueous products (Ekpo et al., 2016) and the study by (Biller et al., 2012) has shown that *C.vulgaris* is capable of utilizing ammonium preferably as nitrogen source rather than nitrate when both nitrogen species are present in a culture medium. This is because it prefers to assimilate ammonium until it is exhausted before utilizing nitrate as nitrate needs to be hydrolysed to ammonium first (Becker, 1994;Proctor, 1957). Phosphate and nitrate in the diluted aqueous products were typically very low compared to the standard media. In conclusion, the limited growth of *C.vulgaris* in these diluted aqueous products is mainly attributed to nutrient limitation rather than toxicity.

8.2.1.4 Biomass Concentration

At the end of the cultivation period, the culture in each bioreactor was harvested by centrifugation, dried and weighed using a weighing scale to obtain the actual biomass produced. The biomass concentrations produced in each 500mL bioreactor as well as volatile content in the biomass have been presented in **Figure 8-11**. It was observed that the quantity of biomass harvested varied with the type of culture media used and also the degree of dilution. Generally the biomass concentration was higher with the catalysed SCWG aqueous product (denoted by '**C**') than the non-catalysed aqueous product (denoted by '**NC**'). Although the control experiment with Bold's Basal medium still had the highest biomass concentration (700 mg/L). In addition, the degree of dilution significantly affected biomass concentration as the lowest dilution of the SCWG aqueous product (1:50) had the highest biomass concentration compared to other dilutions – 1:200 and 1:400. For instance with the catalysed aqueous product at 1:50 dilution, the biomass concentration was 400 mg/L whereas at 1:200 and 1:400 dilution, it was 250 mg/L and 210 mg/L respectively. Microalgal biomass was mainly made up of volatiles as it was between 93-97% for all culture media including the Bold's Basal media. There was no significant change in volatile content with an increase in dilution factor.

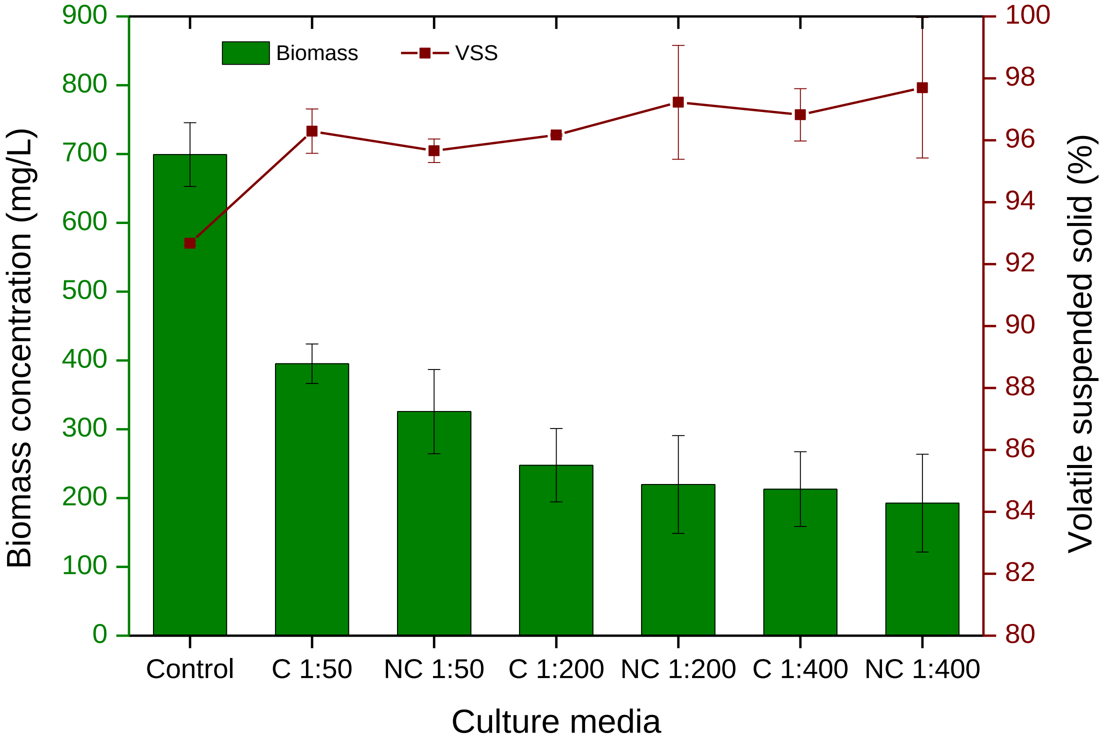


Figure 8-11: Biomass concentration and volatiles from catalysed and non-catalysed SCWG aqueous products using the 500mL bioreactor

Cultivation trial was repeated in a microcultivator using the same aqueous products. As the microcultivator is a more controlled environment for algal growth compared to the open flasks used in the previous cultivation trials, these trials were performed to compare the growth rate, biomass concentrations and volatile content using this equipment. **Figure 8-12** shows the biomass concentration and volatiles obtained after harvesting from the microcultivator. Similar trends were observed using this type of cultivation system. Although higher biomass concentrations were obtained with the microcultivator than the 500mL bioreactors. The volatile content of the grown biomass was between 97-99%. Generally for both cultivation systems, volatile content of *C.vulgaris* biomass using standard BBM was lower 93-95% compared to the SCWG aqueous products.

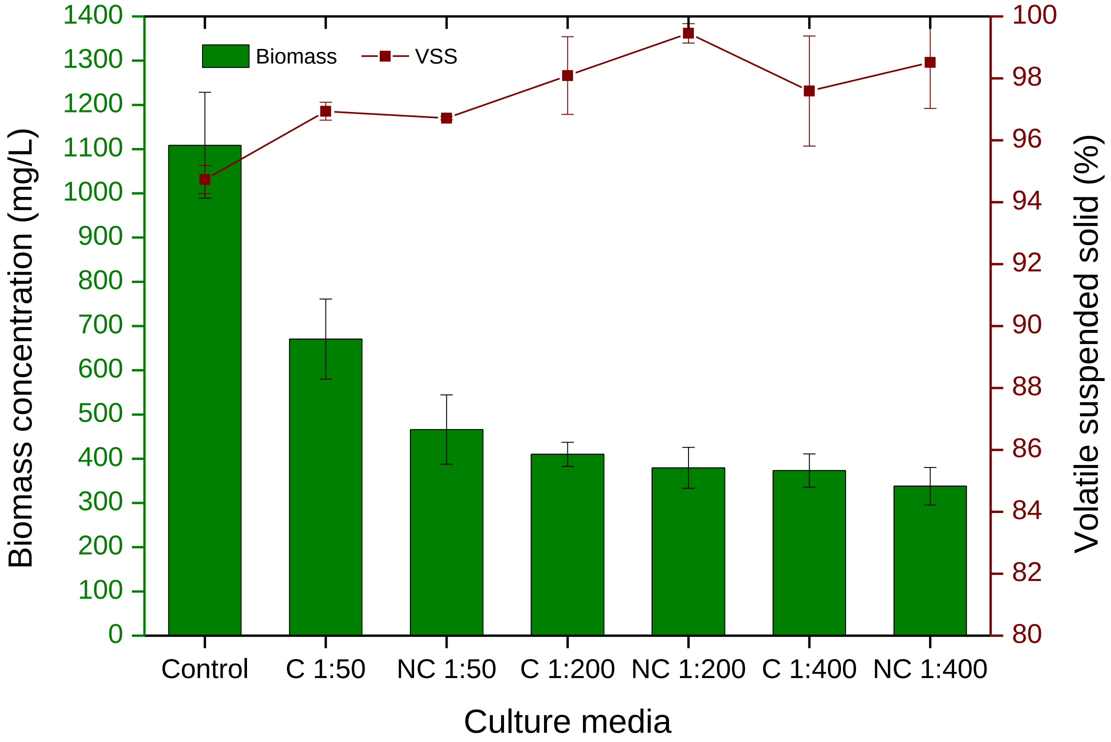


Figure 8-12: Biomass concentration and volatiles from catalysed and non-catalysed SCWG aqueous products using the microcultivator

8.2.2 Using aqueous product from SCWG of various feedstocks

8.2.2.1 Characterisation of aqueous products

The aqueous products from SCWG of *C.vulgaris*, *L.digitata* and sewage sludge were analysed to determine the concentrations of TOC, nitrogen, ammonium, phosphate, potassium, nitrate, acetate and phenols. The results are presented in

Table 8-4. The concentration of species in the aqueous products recovered from SCWG of *C.vulgaris*, *L.digitata* and sewage sludge varied. The levels of TOC in these aqueous products were generally high compared to other species. The highest TOC was obtained from SCWG of *C.vulgaris* (9,190 mg/L) followed by sewage sludge then *L.digitata* (4,180 mg/L). Also the levels of ammonium was particularly high in aqueous product from SCWG of *C.vulgaris* and sewage sludge with concentrations of about 9,810 mg/L and 5,730 mg/L respectively whereas it was lowest in the aqueous product from SCWG of *L.digitata* (360 mg/L). Potassium was highest in the seaweed

(2,420 mg/L) and lowest in sewage sludge (150 mg/L) while acetate levels was between 1,490 mg/L and 2,900 mg/L in all the aqueous products. Phosphate was generally low compared other species while phenol was between 250-360 mg/L.

Table 8-4: Characterisation of aqueous products from SCWG of various biomass

	Concentration (mg/L)			
Species	*C.vulgaris*	*L.digitata*	Sewage sludge	BBM
TOC	9,190	4,180	7,570	-
TN	n/d	530	n/d	40
NH_4^+	9,810	360	5,730	-
PO_4^{3-}	480	40	50	150
K^+	520	2,420	150	80
Acetate	1,490	1,580	2,900	-
NO_3^-	n/d	n/d	n/d	180
Phenols	350	250	360	-

$^{n/d}$ Not determined

8.2.2.2 Cultivation Trials

Cultivation trials was performed with the aqueous products from SCWG of *C.vulgaris*, *L.digitata* and sewage sludge at 1:50, 1:200 and 1:400 dilution using 500mL bioreactors as shown in **Figure 8-13**. The trial was repeated using the microcultivator at the same dilution. The standard Bold's Basal medium was used as the control experiment. The growth of *C.vulgaris* using these two types of cultivation systems was investigated in terms of the final biomass concentration harvested at the end of the cultivation period.

Table 8-5: Concentration of nutrients in the culture media from SCWG of *C.vulgaris*, *L.digitata* and sewage sludge after dilution

	Concentration (mg/L)				
Culture media	TN	NH_4^+	PO_4^{3-}	K^+	NO_3^-
BBM	40	-	150	80	180
C.vulgaris 1:50	n/d	196.2	9.6	10.4	n/d
C.vulgaris 1:200	n/d	49.05	2.4	2.6	n/d
C.vulgaris 1:400	n/d	24.53	1.2	1.3	n/d
L.digitata 1:50	10.6	7.2	0.8	48.4	n/d
L.digitata 1:200	2.65	1.8	0.2	12.1	n/d
L.digitata 1:400	1.33	0.9	0.1	6.1	n/d
Sewage sludge 1:50	n/d	114.6	1	3	n/d
Sewage sludge 1:200	n/d	28.7	0.25	0.75	n/d
Sewage sludge 1:400	n/d	14.3	0.13	0.38	n/d

$^{n/d}$ Not determined

Figure 8-13: *C.vulgaris* growing in diluted SCWG aqueous products from microalgae, *L.digitata* and sewage sludge

8.2.2.3 Growth Kinetics

Data from both the turbidity and pH measurements of the various batch two cultures over a two week cultivation period are presented in **Table 8** in **Appendix 3**. Based on these data, the growth curves in each culture media as well as the corresponding change in pH with time have been shown in **Figure 8-14** to **Figure 8-23**. Also the specific growth rate of the culture during the lag, exponential and stationary phases in each of these bioreactors are presented in **Table 8-6**.

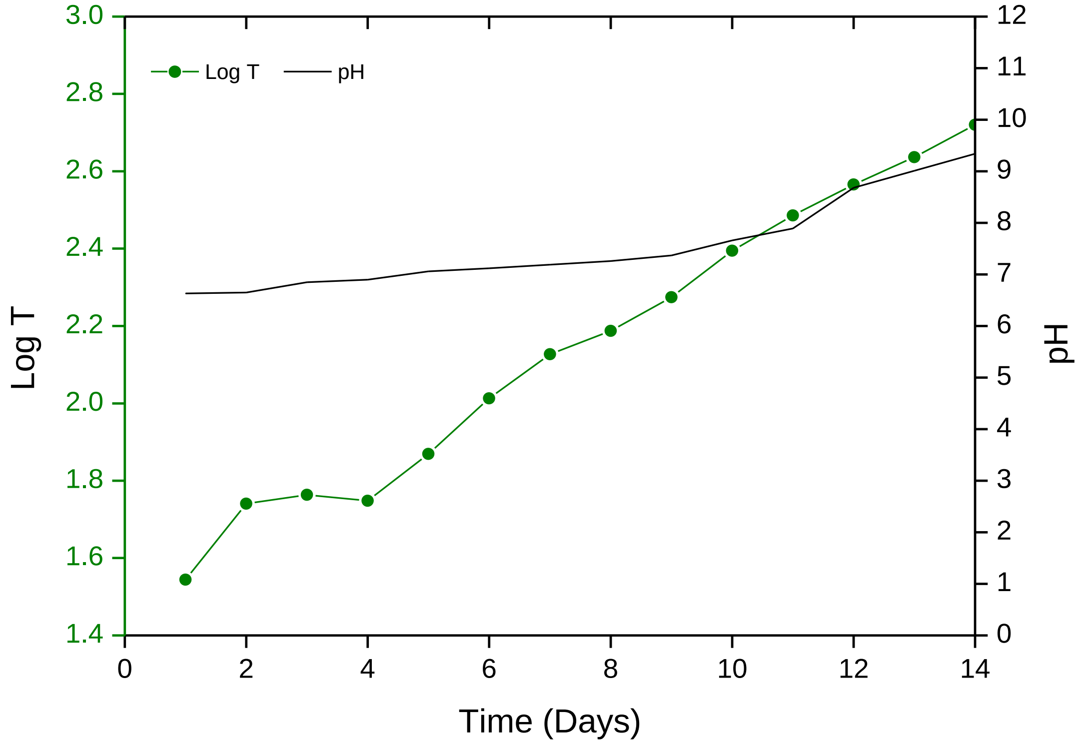


Figure 8-14: Growth Phases and pH change in Standard Bold's Basal Medium

Figure 8-14 shows a fast growing culture in the standard Bold's Basal media which was used as the control experiment. It was observed that there was no lag period; instead the culture proceeded to the exponential phase growing at 0.13 day^{-1} until day 7. The growth rate reduced to 0.09 day^{-1} at the later exponential phase until day 14 which marks the beginning of the stationary phase. During the growth period, the pH increased from 6.63 to 9.34 at day 14 which implies that the culture was still growing at this time.

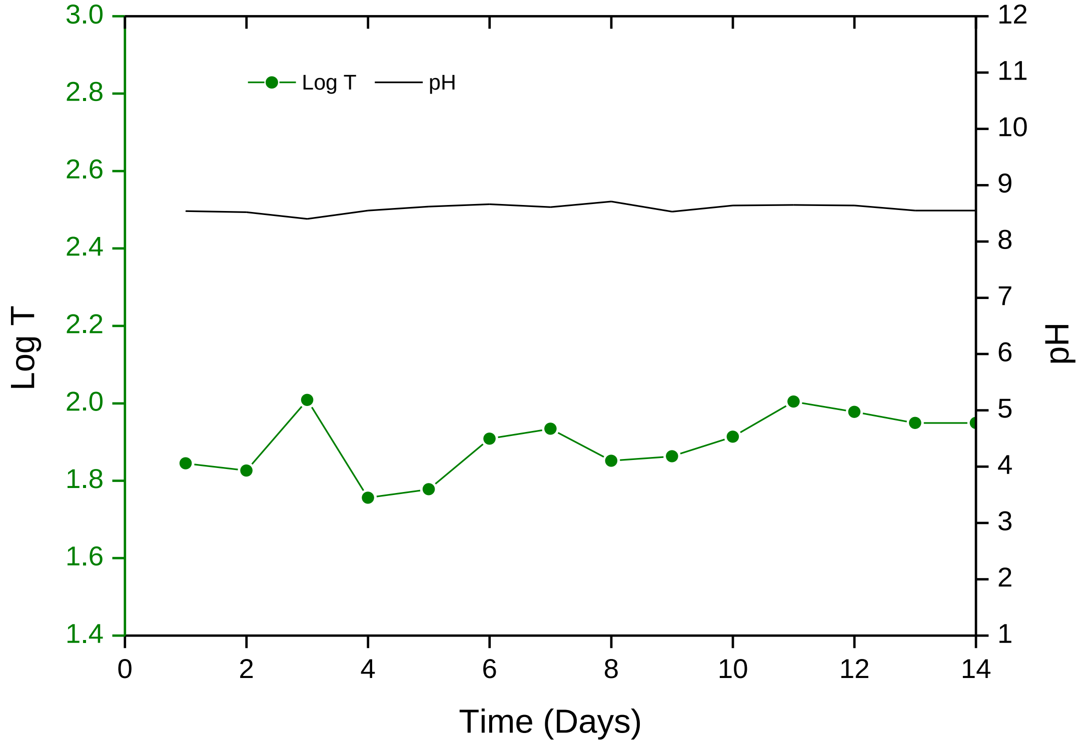


Figure 8-15: Growth Phases and pH change in aqueous product from SCWG of *C.vulgaris* at 1: 50 dilution

Figure 8-15 shows the growth of *C.vulgaris* in the SCWG aqueous product from *C.vulgaris* diluted at 1:50. The growth curve shows an abnormal trend with no clear distinction between the various stages of growth- lag phase, the exponential phase and the stationary phase. The culture may have been dying off due to inhibitory effect of some species at this dilution as there was also no significant change in pH throughout the cultivation period.

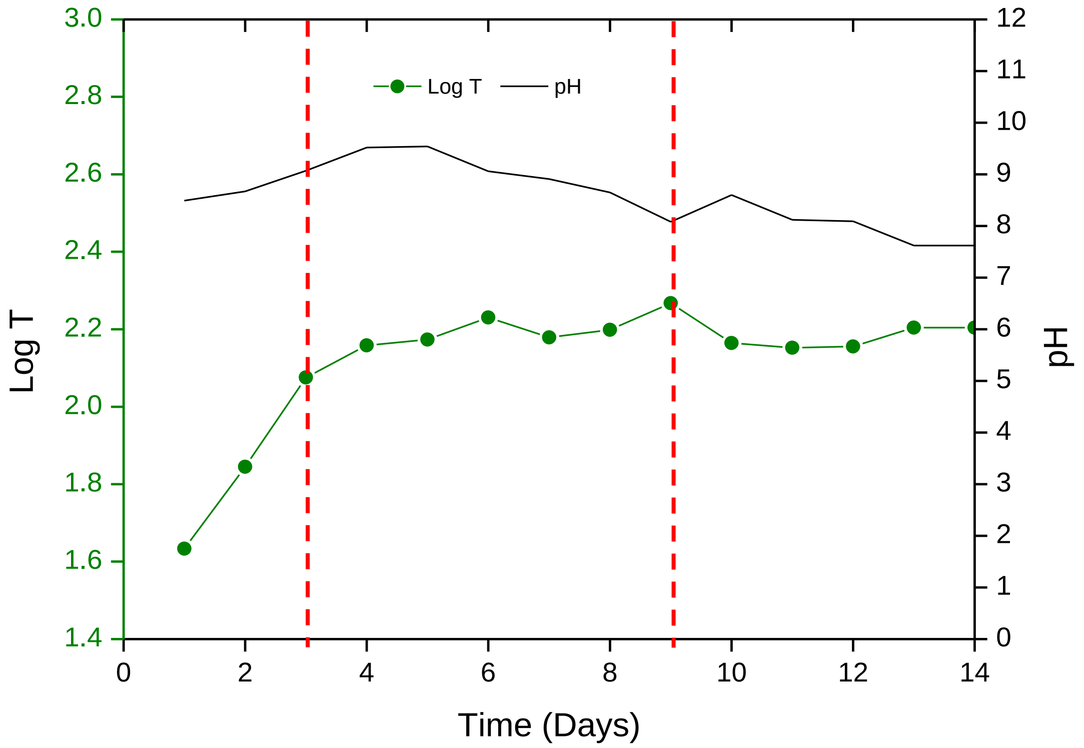


Figure 8-16: Growth Phases and pH change in aqueous product from SCWG of *C.vulgaris* at 1: 200 dilution

Figure 8-16 shows the growth of *C.vulgaris* in the aqueous product from SCWG of *C.vulgaris* diluted at 1:200. There was no lag phase in growth instead the growth was exponential for the first 3 days at 0.22 day^{-1} which reduced to 0.05 day^{-1} afterwards until day 9 when it started approaching stationary phase. During the cultivation period, the pH changed significantly over time gradually increasing from 8.49 to about 9.54 by day 5 and decreased gradually fluctuating periodically until day 14 when it became 7.62.

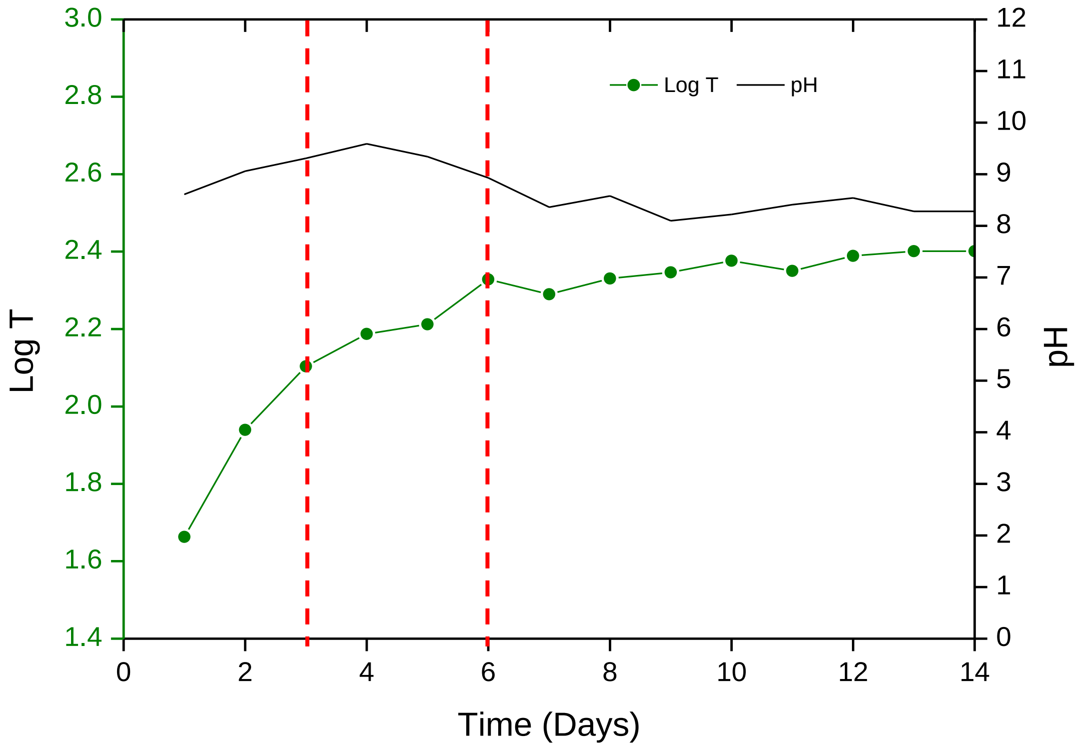


Figure 8-17: Growth Phases and pH change in aqueous product from SCWG of *C.vulgaris* at 1: 400 dilution

Figure 8-17 shows the growth curve and pH change in the culture grown in the aqueous product from SCWG of *C.vulgaris* which was diluted to 1:400. There was also no lag phase and the exponential phase also lasted for the first 3 days with specific growth rate of 0.22 day^{-1} followed by a gradual decrease in growth rate (0.07 day^{-1}) until day 6. Afterwards the growth significantly decreased as it approached the stationary phase which corresponds to a fairly constant pH of 8.1-8.3 after day 9.

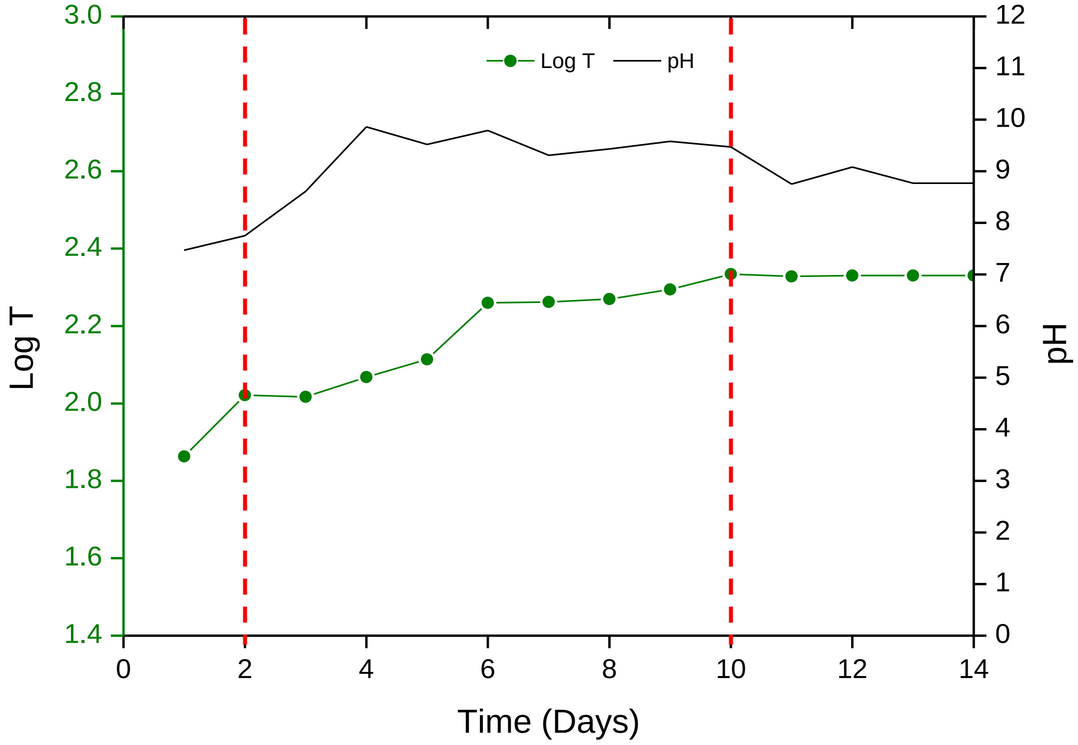


Figure 8-18: Growth Phases and pH change in aqueous product from SCWG of *L.digitata* at 1: 50 dilution

Figure 8-18 shows the growth curve and pH change in the culture grown in the aqueous product from SCWG of *L.digitata* which was diluted to 1:50. The exponential phase only lasted for 2 days with specific growth rate of 0.16 day^{-1} after which the growth rate reduced gradually to 0.05 day^{-1} until day 10. During this time, the pH increased from 7.47 to 9.47. The stationary phase began after day 10 and the specific growth further reduced to 0.02 day^{-1} with a fairly constant pH till the end of the cultivation period.

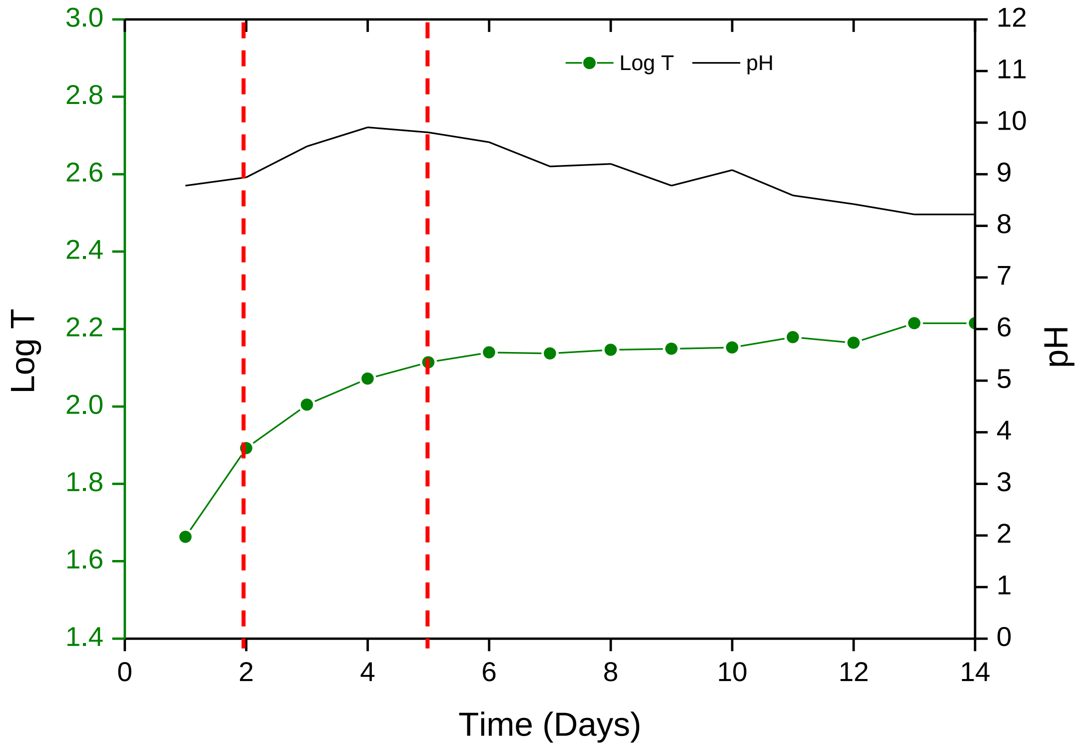


Figure 8-19: Growth Phases and pH change in aqueous product from SCWG of *L.digitata* at 1: 200 dilution

Figure 8-19 shows the growth curve and pH change of the culture grown in the aqueous product from SCWG of *L.digitata* which was diluted to 1:200. Rapid growth occurred in the first 2 days at 0.23 day^{-1} while the specific growth rate reduced afterwards to 0.05 day^{-1} until day 5 which is the beginning of the stationary phase. The specific growth rate during the stationary phase was 0.01 day^{-1} until the end of the cultivation period. The pH increased from 8.78 to 9.91 during the first 4 days and began decreasing to 9.08 at day 10 and even lower as the culture approached the stationary phase.

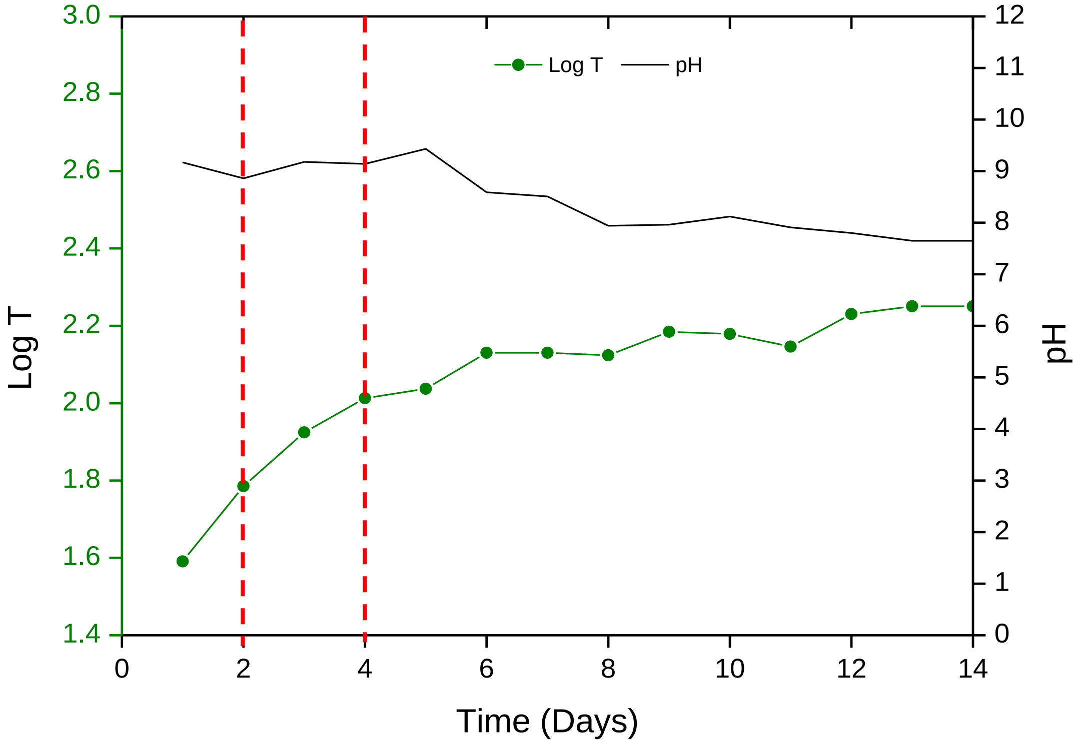


Figure 8-20: Growth Phases and pH change in aqueous product from SCWG of *L.digitata* at 1: 400 dilution

Figure 8-20 shows the growth curve and pH change in the culture grown in the aqueous product from SCWG of *L.digitata* which was diluted to 1:400. The culture showed rapid growth (0.19 day^{-1}) during the first 2 days while the growth rate reduced gradually to 0.11 day^{-1} until day 4 when the stationary phase began. During the stationary phase, the specific growth rate reduced to 0.03 day^{-1} until the end of the cultivation period. During this cultivation period, the pH reduced from 9.17 to 7.91 but remained fairly constant afterwards as the culture approached the stationary phase.

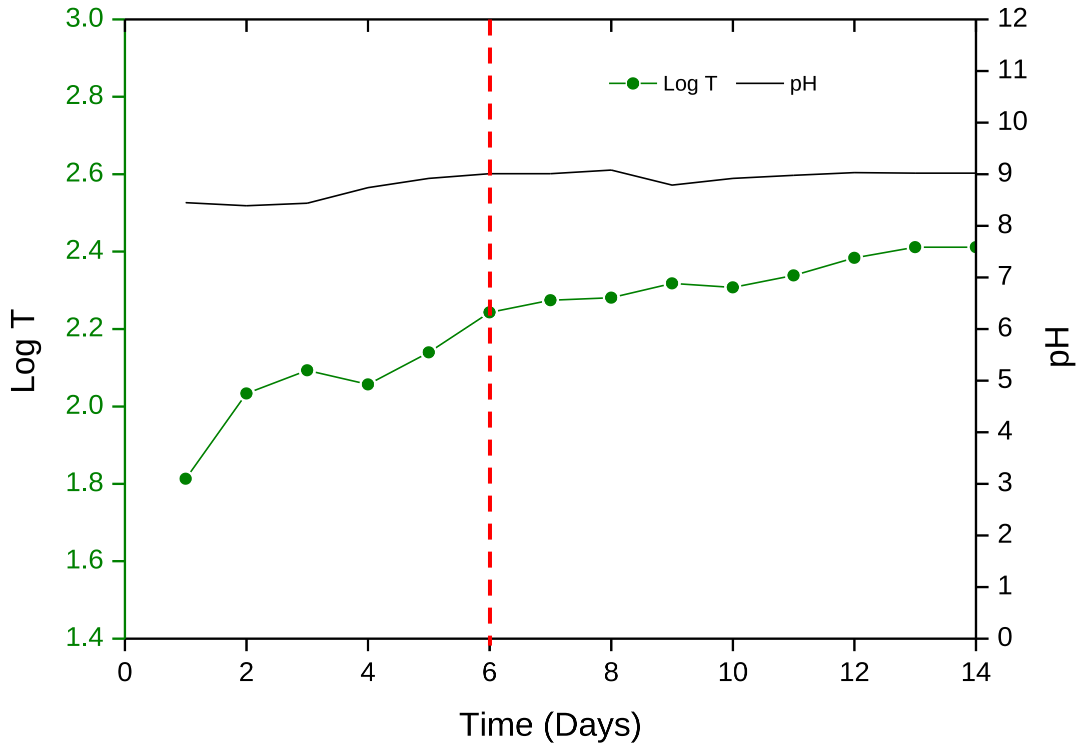


Figure 8-21: Growth Phases and pH change in aqueous product from SCWG of sewage sludge at 1: 50 dilution

Figure 8-21 shows the growth curve and pH change in the culture grown in the aqueous product from SCWG of sewage sludge which was diluted to 1:50. This culture exhibited rapid growth in the first 2 days with specific growth rate of 0.22 day^{-1} which reduced to 0.05 day^{-1} by day 6. Afterwards, the culture grew at a steady slow rate of 0.02 day^{-1} until the end of the cultivation period. Throughout the growth period, the pH changed from 8.45 to 9.02.

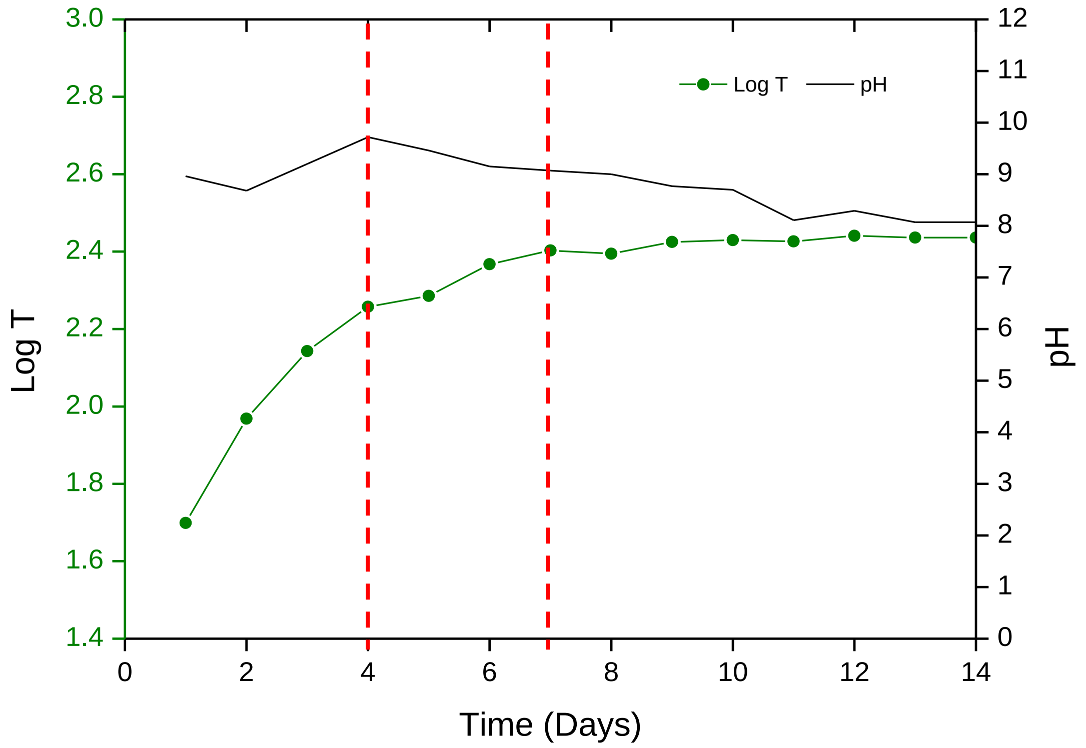


Figure 8-22: Growth Phases and pH change in aqueous product from SCWG of sewage sludge at 1: 200 dilution

Figure 8-22 shows the growth curve and pH change in the culture grown in the aqueous product from SCWG of sewage sludge which was diluted to 1:200. Exponential growth occurred within the first 4 days initially at 0.27 day^{-1} and later reduced to 0.14 day^{-1} with pH increasing from 8.96 to 9.72. Between day 4 and day 7, the growth rate further reduced to 0.05 day^{-1} while the pH reduced to 9.07. The stationary phase began after day 7 while the pH was fairly constant until the end of cultivation period.

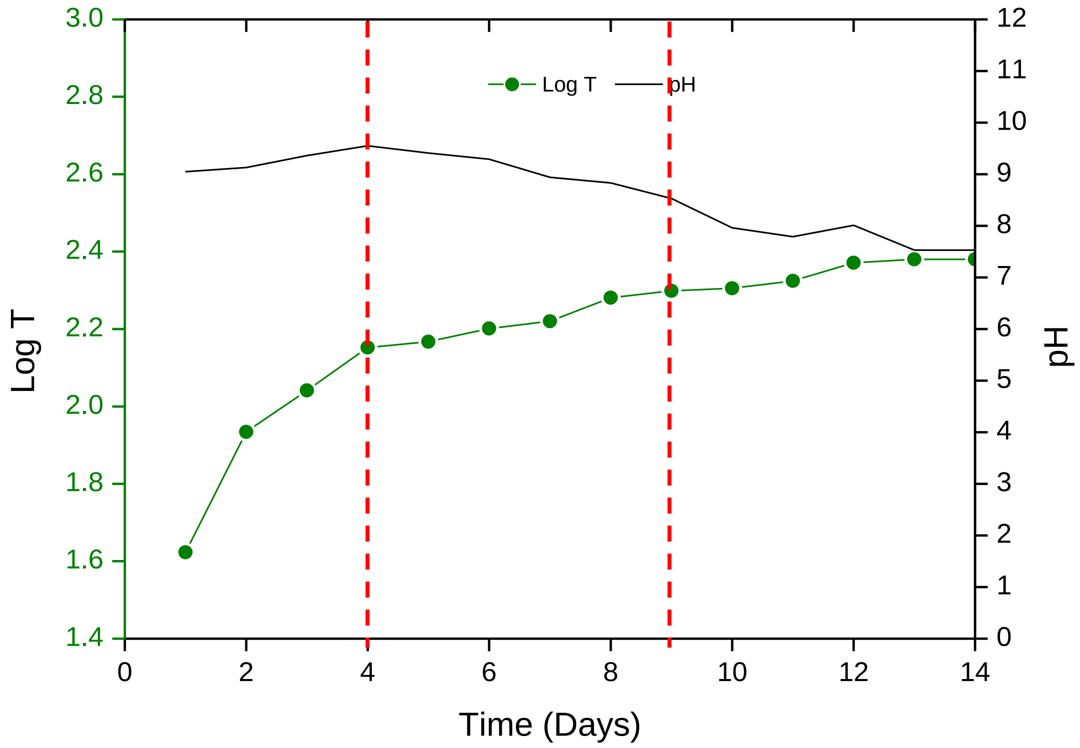


Figure 8-23: Growth Phases and pH change in aqueous product from SCWG of sewage sludge at 1: 400 dilution

Figure 8-23 shows the growth curve and pH change in the culture grown in the aqueous product from SCWG of sewage sludge which was diluted to 1:400. Rapid growth occurred within the first 4 days with initial growth rate of 0.31 day^{-1} which reduced to 0.11 day^{-1}. The growth rate further reduced to 0.03 day^{-1}during the stationary phase until the end of cultivation period. During the growth period, the pH changed significantly from 9.05 to 8.01 and remained fairly constant at stationary phase.

Table 8-6: Summary of *C.vulgaris* specific growth rate in SCWG aqueous products from various feedstocks

Culture Media	Specific Growth Rate (day^{-1}) Lag Phase	Early Exponential phase	Later Exponential phase	Early Stationary phase	Later Stationary phase
Standard BBM	*	0.13	0.09		
C.vulgaris 1:50	**	**	**	**	**
C.vulgaris 1:200	*	0.22	0.05	0.01	
C.vulgaris 1:400	*	0.22	0.07	0.01	
L.digitata 1:50	*	0.16	0.05	0.02	0.001
L.digitata 1:200	*	0.23	0.05	0.01	
L.digitata 1:400	*	0.19	0.11	0.03	0.01
Sewage sludge 1:50	*	0.22	0.05	0.02	
Sewage sludge 1:200	*	0.27	0.14	0.05	0.002
Sewage sludge 1:400	*	0.31	0.11	0.03	0.02

*No lag phase

**No distinct growth phase

Table 8-6 summarizes the individual growth rates during the lag, exponential and stationary phases of *C.vulgaris* in the various bioreactors (**Figure 8-14** to **Figure 8-23**). In the standard Bold's Basal medium, *C.vulgaris* maintained exponential growth at the start of cultivation until the end of the cultivation period (day 14). Rapid growth in the standard medium occurred within the first 7 days whereas in other diluted SCWG culture media, rapid growth occurred only within the first 2-3 days. In the later exponential phase, the growth rate of the culture reduced significantly in most of the culture media. In most bioreactors, *Chlorella vulgaris* showed significant growth except for the aqueous product from SCWG of *Chlorella* at 1:50 dilution which may be due to inhibition from higher concentrations of ammonium as shown in **Table 8-5**. As stated by (Biller et al., 2012), other growth inhibitors include nickel, phenols and fatty acids. Generally lower growth rates of culture in diluted aqueous products from SCWG of *L.digitata* could be as a result of nutrient limitation rather than toxicity. Compared to diluted SCWG aqueous products from *C.vulgaris* and sewage sludge, diluted aqueous products from SCWG of *L.digitata* had lower nutrients as shown in **Table 8-5**.

8.2.2.4 Biomass Concentration

At the end of the cultivation period, the cultures were harvested by centrifugation, dried and weighed using a weighing scale to obtain the actual biomass produced after cultivation. **Figure 8-24** shows the individual biomass concentrations produced during the growth trials as well as the volatile suspended solids.

It was observed that the quantity of biomass obtained were different with each culture media and with each dilution. For SCWG of *C.vulgaris* denoted by '**C**', the highest biomass (260mg/L) was obtained with the 1:200 dilution followed by 1:400 dilution having 220mg/L. The least biomass was obtained with the 1:50 dilution. With the aqueous product from *L. digitata* denoted by '**L**', 1:50 dilution gave the highest biomass concentration (230mg/L) while similar biomass concentrations between 120-130mg/L were obtained with the 1:200 and 1:400 dilution. Also with the aqueous product from sewage sludge denoted by '**SS**', the highest biomass was obtained with the 1:50 dilution having about 340mg/L. The biomass from **SS** 1:50 was the highest among other culture media used including the control media (330mg/L). Biomass concentration was 230mg/L and 180mg/L for the **SS** 1:200 and **SS** 1:400 dilution respectively. The volatile suspended solids in the cultures harvested from the SCWG aqueous products were fairly similar ranging from 96% to 99% for all dilutions and were found to be higher compared to the volatile content in the harvested biomass from the standard bold media (89%).

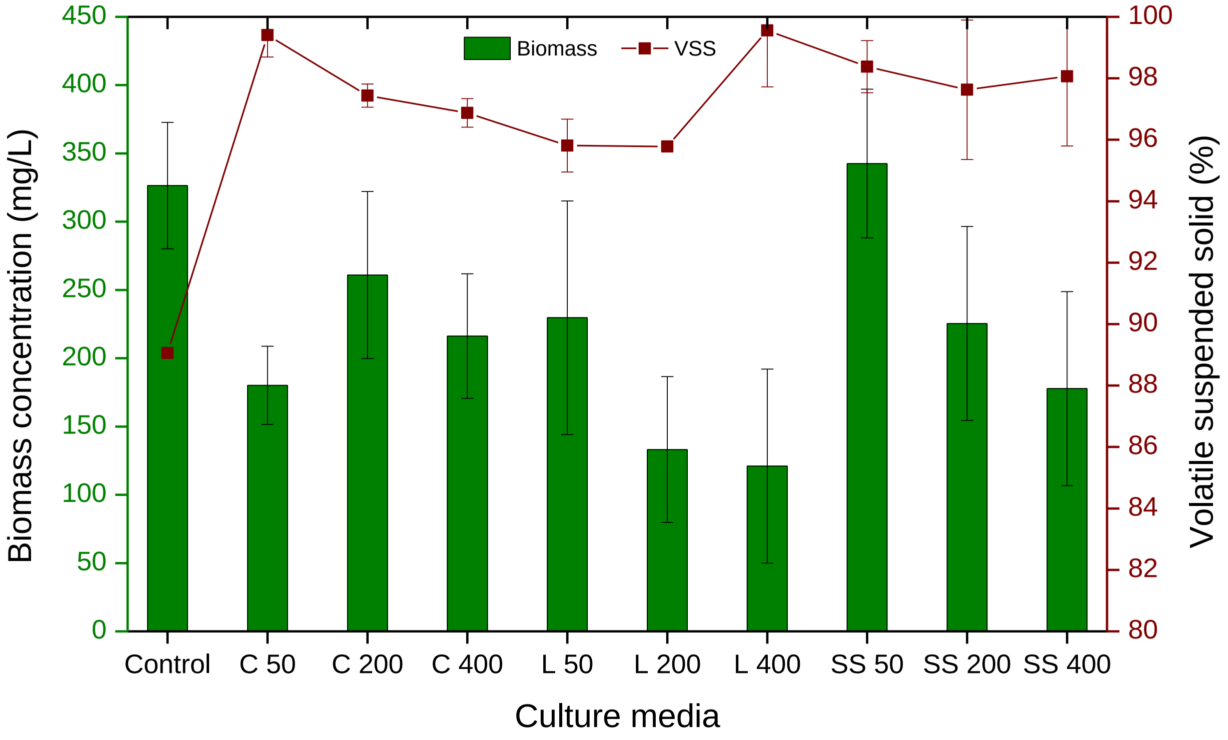


Figure 8-24: Biomass concentration and volatiles using SCWG aqueous products from various feedstocks at different dilutions

8.3 Physical Recovery of phosphorus by adsorption on biochar

In a previous study by (Takaya et al., 2016b), biochars pre-treated with magnesium salts were found to significantly improve phosphate removal efficiency from aqueous solutions. The Mg-treated oak biochar improved phosphate adsorption from 3.6% (in untreated oak biochar) to 70.3%. Therefore in this study, Mg-treated oak biochar was used as a suitable adsorbent material. Physical recovery of phosphorus by adsorption onto a Mg-treated biochar was performed in various batches using the aqueous products recovered hydrothermal processing of swine manure at 120°C, 170°C, 200°C and 250°C with H_2SO_4 additive (stated in **Chapter 5**). The high reactive phosphorus in solution with mineral acid treatment in the form of inorganic-P is very important and constitutes a major fraction of recoverable P (Szogi et al., 2015). Aqueous products recovered from the mineral acid (H_2SO_4) treatment contained higher phosphate levels compared to aqueous products recovered from using other additives, therefore they were utilised for this study.

The adsorption test was conducted using varying concentrations (250 mg/L, 500 mg/L, 750 mg/L and 1000 mg/L) of these aqueous products at pH 7. At these lower concentrations, the pH was acidic and even more acidic with the 1000 mg/L aqueous product. In order to conduct the adsorption test, the pH was adjusted to 7 using 0.1M HCl and 0.1M NaOH. Adjusting the pH with these reagents, resulted in a higher degree of dilution, making the set concentration of 250mg/L, 500mg/L, 750mg/L and 1000mg/L to deviate into a lower concentration of phosphate. However the results obtained from this scoping study were useful and presented in **Section 8.3.1.**

The result from the scoping study gave an insight on the maximum concentration required for an efficient phosphate adsorption. The second phase of adsorption was performed at higher pH- 8 and 9 at a concentration of 250 mg/L and the adsorption efficiency results were compared with those obtained at pH 7. Lastly, SEM and EDX images of a selection of the adsorbed biochars were analysed to determine the presence of phosphate-compounds. The images were compared to the Mg-treated biochar which was initially used for adsorption.

8.3.1 Effect of varing concentration on phosphate adsorption

Table 8-7 shows the quantity of phosphate adsorbed and the removal efficiency using the various aqueous products. It was observed that the quantity of phosphate adsorbed increased with an increase in phosphate concentration for all aqueous products. However it was vice versa in terms of the removal efficiency. Higher removal efficiencies between 83-92% were observed at the lowest concentration investigated which was between 69-140 mg/L.

Table 8-7: Phosphate adsorption using aqueous products from thermal hydrolysis and HTC at pH 7

Initial Concentration of aqueous product	Final Concentration at pH 7	Quantity of phosphate adsorbed (mg/g)	Removal Efficiency (%)
120°C H_2SO_4			
250 mg/L	140	58	83
500 mg/L	307	123	80
750 mg/L	441	175	79
1000 mg/L	553	219	79
170°C H_2SO_4			
250 mg/L	69	32	92
500 mg/L	143	54	75
750 mg/L	215	77	72
1000 mg/L	272	84	62
200°C H_2SO_4			
250 mg/L	85	37	86
500 mg/L	173	61	71
750 mg/L	258	87	67
1000 mg/L	351	117	67
250°C H_2SO_4			
250 mg/L	98	42	85
500 mg/L	196	76	77
750 mg/L	287	109	76
1000 mg/L	387	147	76

8.3.2 Effect of varing pH on phosphate adsorption

The results presented in **Table 8-7** show that at pH 7, higher phosphate removal was achieved with the lowest concentration (250 mg/L). **Figure 8-25** compares phosphate removal efficiency using this concentration at varying pH. Generally, the results indicate higher phosphate adsorption at higher pH irrespective of the type of aqueous product used – from hydrolysis or from hydrothermal carbonisation. For the hydrolysis aqueous product (120°C), similar adsorption efficiencies about 96% were observed at pH 8 and pH 9 which was 13% higher that the removal efficiency observed at pH 7. Also increasing pH from 7 to 9, removed about 2%, 6% and 10% more phosphate in the aqueous product from hydrolysis 170°C, HTC 200°C and HTC 250°C respectively. Comparing the removal efficiencies at pH 8 and pH 9, there was little increase between 2-4% for most of the aqueous products. In the study by Wunderlich et al., (2015), higher phosphorus removal (98%) and 50% nitrogen was achieved with the addition of magnesium to biochar at pH between 9 and 10. They observed little removal at neutral pH even when magnesium was added. They concluded that the adsorption process is controlled by pH. The results obtained by Wunderlich et al., (2015) agree with the results in this study as phosphorus removal with Mg-treated oak biochar was between 90-96%. Previous studies have shown that biochar is a poor adsorbent material unless it is impregnated with cation (Yao et al., 2013).

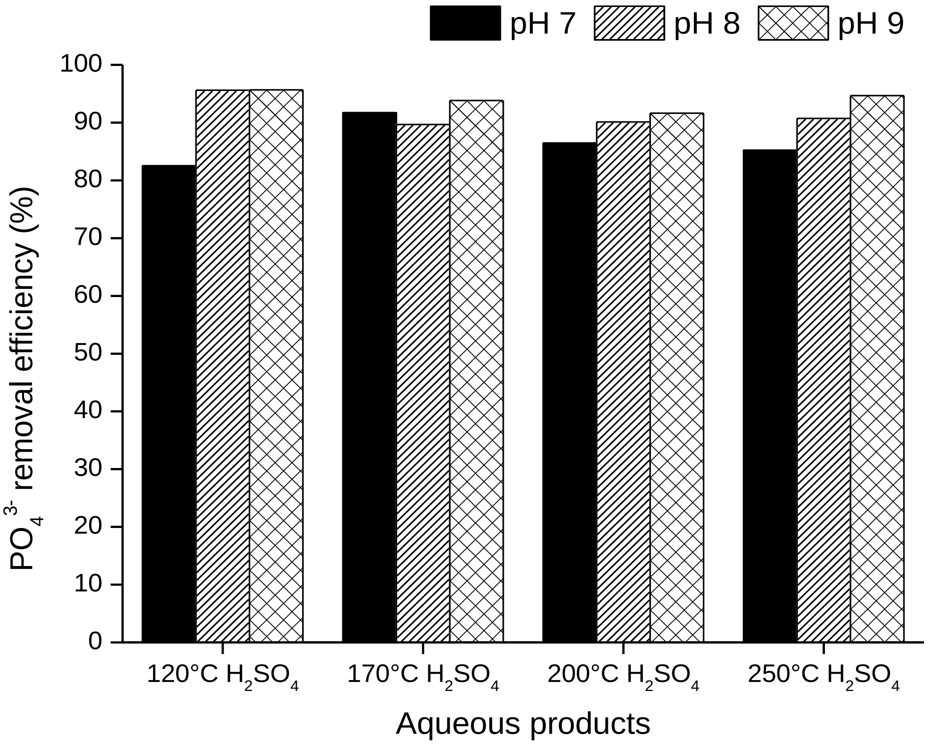


Figure 8-25: Comparison of pH using 250 mg/L H_2SO_4 aqueous products

8.3.3 Analysis of Mg-treated biochar and adsorbed biochars

The SEM images and the relative composition from EDX analysis for pure compounds of calcium phosphate and struvite are shown in **Figure 8-26** and **Figure 8-27** respectively. Also SEM and EDX analysis of the Mg-treated biochar and a typical adsorbed char is shown in some selected adsorbed chars are shown in **Figure 8-28** and **Figure 8-29** respectively. SEM and EDX analysis of all other adsorbed chars are presented in **Appendix 3**. **Table 8-8** shows the elemental composition in the various adsorbed chars comparing them with the composition in the pure compounds and the modified biochar before adsorption.

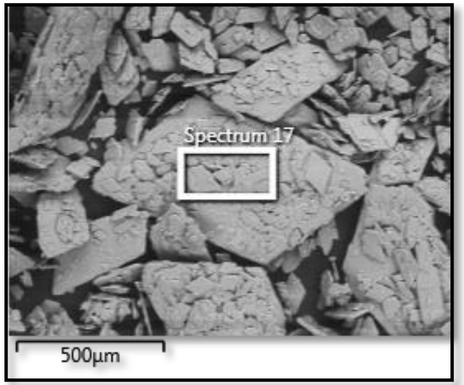
Table 8-8: Summary of elemental composition in pure compounds, Mg-modified biochar and the various adsorbed chars

		Elemental Composition (%)			
Sample		Ca	P	N	Mg
Calcium phosphate		9.63	17.51	-	-
Struvite ($MgNH_4PO_4.6H_2O$)		-	12.95	14.48	11.68
Mg-Modified biochar		0.14	-	-	4.99
120°C H_2SO_4	pH 7	2.87	2.73	-	2.40
170°C H_2SO_4	pH 7	2.76	2.44	-	1.64
200°C H_2SO_4	pH 7	4.39	3.36	-	1.93
250°C H_2SO_4	pH 7	1.38	1.00	-	4.28
250°C H_2SO_4	pH 8	5.05	3.86	-	1.66
250°C H_2SO_4	pH 9	3.50	3.09	-	3.57
250°C H_2SO_4	no pH	0.06	-	-	3.59

It was observed that the main elements present in the calcium phosphate standard were Ca (10%), P (18%) and O (73%) while the struvite compound was mainly composed of N (14%), O (61%), Mg (12%) and P (13%). The Mg-treated biochar contained significant quantities of Mg (5%) which is most likely present from the pre-treatment of the oak derived biochar with $MgCl_2$. It also contained very high carbon (86%) which is a characteristic of biochars obtained from pyrolysis process. Insignificant amounts of Fe, Cl, Ca, S between 0.05-0.4% were also present however no traces of phosphorus was detected. The composition of Mg in the adsorbed biochars were relatively constant between 2-4% for all conditions which implies that change in pH or type of process water used did not affect its adsorption.

Using aqueous products from hydrolysis and HTC at pH 7 as shown in **Table 8-8**, it was observed that Ca content increased from 0.1% in the raw biochar to between 1-4% in the adsorbed biochars. Also, phosphorus was present in the adsorbed biochars increasing to about 1-3% compared to the raw biochar which had no traces.

Using aqueous product from HTC 250°C alone as shown in **Table 8-8**, calcium content in the adsorbed biochars increased to 1%, 5% and 4% at pH 7, pH 8 and pH 9 respectively while the composition of Ca remained the same in the adsorbed char with no change in pH. On the other hand, phosphorus content in the adsorbed biochars increased with increasing pH with the least (1%) at pH 7 and between 3-4% at higher pH. There was no detection of phosphorus in the biochar with no pH adjustment. These results indicate the formation of calcium phosphate in the biochars during adsorption as there were no traces of either nitrogen or magnesium in any of the adsorbed biochars which indicate the formation of struvite. Adsorption using the aqueous product from HTC 250°C without any pH adjustment (with starting pH of 3.95) showed there was no formation of calcium phosphate as an increase in pH favours its formation.



Element	Atomic %
O	72.86
P	17.51
Ca	9.63
Total:	100.00

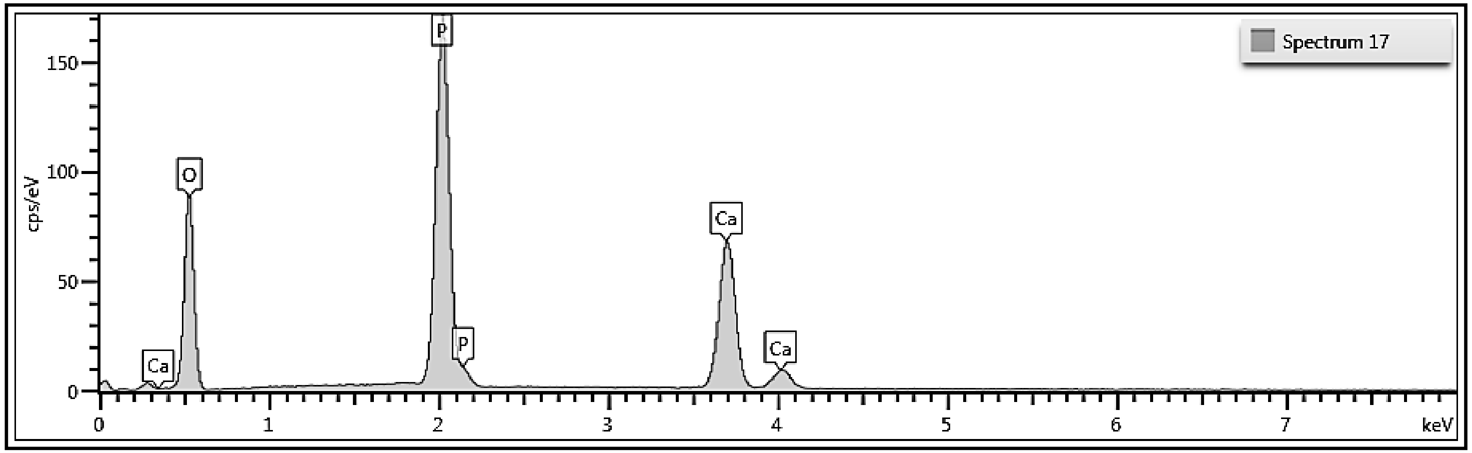
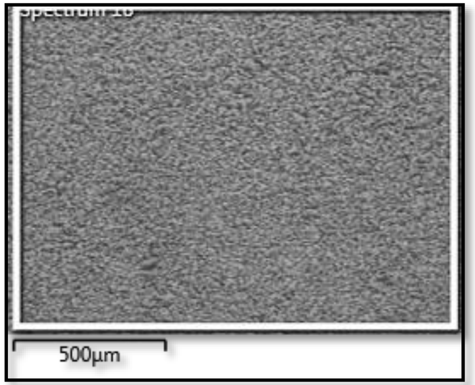


Figure 8-26: Calcium phosphate



Element	Atomic %
N	14.48
O	60.89
Mg	11.68
P	12.95
Total:	100.00

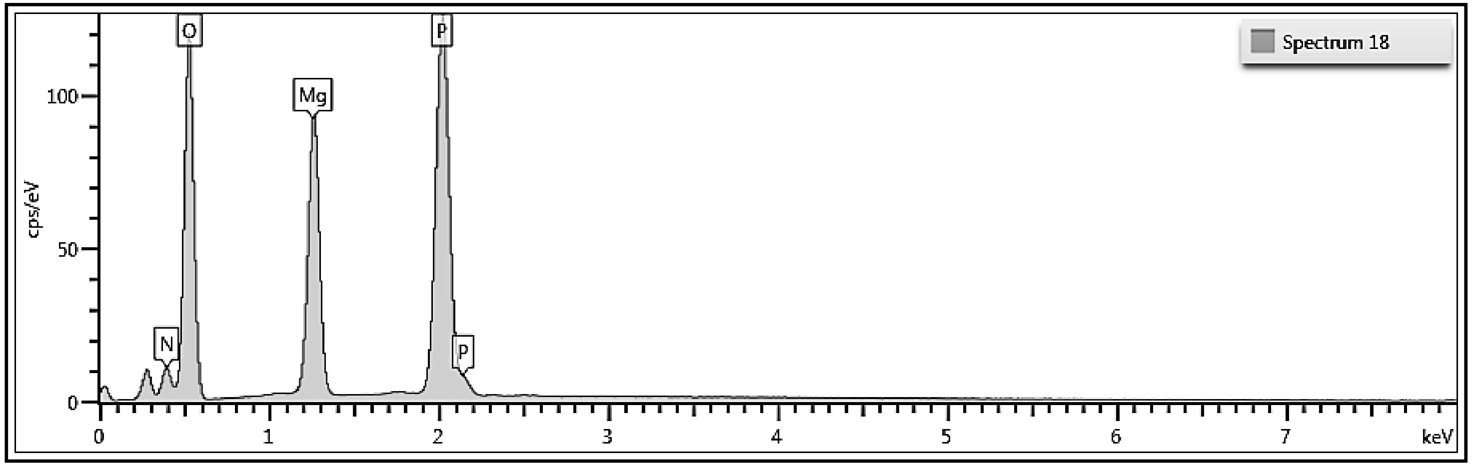
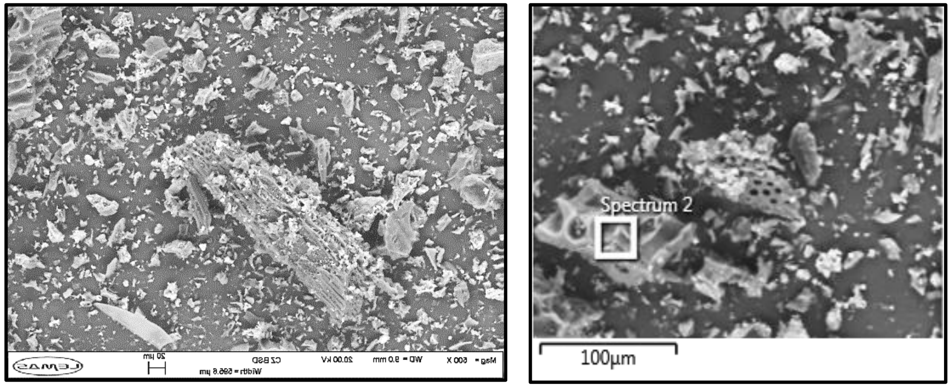


Figure 8-27: Struvite compound ($MgNH_4PO_4.6H_2O$)



Element	Atomic %
C	85.60
O	8.57
Mg	4.99
S	0.05
Cl	0.37
Ca	0.14
Fe	0.23
Cu	0.06
Total:	100.00

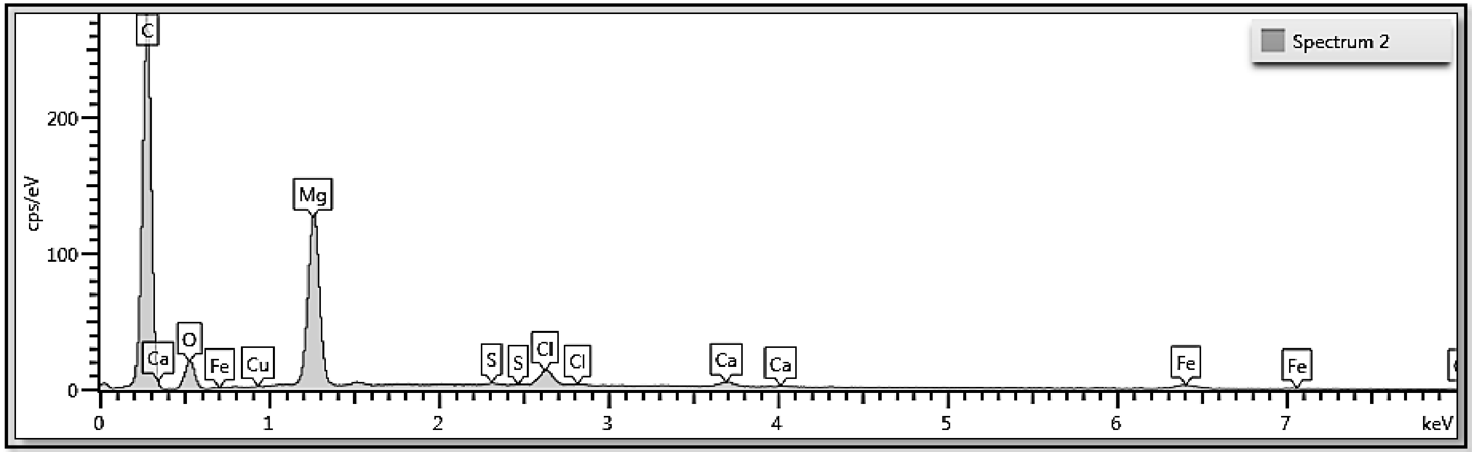


Figure 8-28: The modified Mg-treated biochar

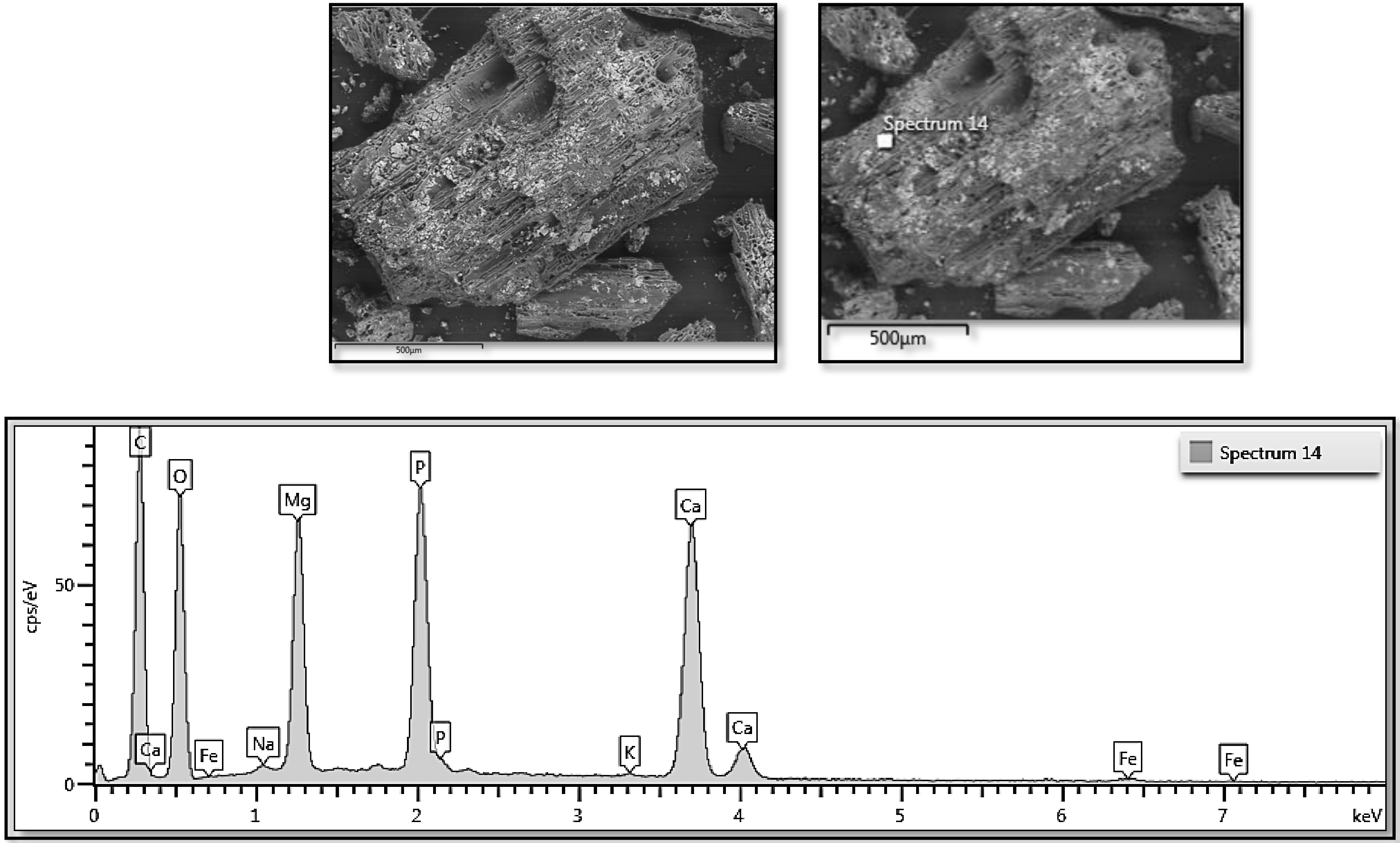


Figure 8-29: Typical SEM and EDX elemental composition of an adsorbed biochar

8.4 Conclusion

Generally for most cultivation trials, *Chlorella vulgaris* showed significant growth except for the aqueous product from SCWG of *Chlorella* at 1:50 dilution which may be attributed to inhibitory effect of nickel, phenols, fatty acids as reported by (Biller et al., 2012). In a previous study by Biller et al., (2012), although they performed cultivation trials using HTL aqueous product, it was observed that *Chlorella* preferred utilising ammonium in the aqueous product as a source of nitrogen rather than nitrate. A similar observation was reported by Chen et al., (2011). They also observed that acetate was readily consumed at all dilutions and noticed that at higher dilutions 1:400, there were insufficient nutrients in the culture media to promote growth. The main limiting nutrients for *Chlorella* are nitrogen and potassium while acetate is mainly consumed during heterotrophic or mixotrophic growth (Biller et al., 2012). Overall, the biomass obtained from 1:50 dilution of catalysed SCWG of *S.latissima*, *L.digitata*, sewage sludge and 1:200 *Chlorella* were comparable with the biomass obtained with Bold Basal Media. The recovered biomass could be used for biodiesel production or for lipid extraction.

Experiment conducted on physical recovery by adsorption showed that adsorption of phosphate is significantly affected by concentration as higher removal efficiencies were observed at lower concentrations. In this case the highest removal efficiencies were observed with 250mg/L phosphate. As typical concentrations of phosphate in the aqueous product from hydrothermal treatment of swine manure is many folds higher than threshold concentration, adsorption with biochar should be a secondary stage phosphate recovery method. It is suggested that these liquid waste streams from (TH or HTC) should be used as feedstock in HTL or SCWG and subsequently adsorption of phosphate from the aqueous product obtained after the process is feasible.

Higher adsorption was achieved at higher pH of 8 and 9 compared to pH 7 forming more calcium phosphate in the adsorbed biochars as the pH increases. Consequently, there is no adsorption of phosphate at lower pH (acidic) conditions. There is no likelihood of struvite formation as traces of nitrogen were not detected while the composition of Mg remained constant in all the adsorbed biochars. However further investigation with XRD is needed to confirm this. Overall, the results on phosphorus recovery by adsorption suggests that this technique could be integrated with mineral acid hydrothermal processing and could be adapted in manure management.

Chapter 9 Conclusion and Future Recommendation

9.1 Introduction

The introduction of this thesis identifies the current challenges facing the fertiliser industry due to limited availability of raw materials such as phosphorus from phosphate rocks, increasing demand and food security. As majority of phosphorus is mined from phosphate rocks which are non-renewable sources, there has been increased research in the aspect of nutrient recycling from renewable sources. Another drawback in fertiliser production is that it is an energy intensive process.

An assessment of the literature in combination with experimental work performed for this research leads to the conclusion that extraction of nutrients is dependent on feedstock composition, processing temperature and pH while recovery of phosphorus is dependent on the concentration as well as pH. The concept of a closed loop system of nutrient recovery from by-products of various hydrothermal processing routes have been introduced. This involves biological recovery of nutrients mainly nitrogen in the form of ammonium using microalgae, phosphorus recovery by precipitation and adsorption using aqueous waste streams with high P-extraction and utilization of low-P waste streams during SCWG which yield aqueous by-product rich in nitrogen for microalgae cultivation. The looping also incorporates CO_2 from HTC and HTL for enhanced algae growth and suggests end use of solid and biocrude products.

9.2 Experimental Conclusions

The selection of feedstocks used in this study represents a range of the major problematic wastes which are generated in large quantities and pose a potential threat to the environment. They are mostly known to have high nutrient, high moisture content, and high degradation rate which increases disposal cost using conventional waste management techniques, but make them ideal feedstocks for hydrothermal processing with the aim of nutrient recycling.

Prior to hydrothermal processing, characterisation of these feedstocks by investigating a variety of parameters give an overview of their compositions and potential as feedstocks for nutrient recycling via hydrothermal processing.

In line with the research objectives outlined in **Chapter 1**, the following conclusions have been deduced.

Objective 1:

- Feedstocks behave differently during low temperature and high temperature hydrothermal processing with the composition and yields of by-product depending largely on the feedstock composition and processing temperature.
- The highest solid yields are obtained at the lowest temperature. About 45-60% solid yields from most feedstocks and 80% from digestate.
- Breakdown of organics occur with increasing temperature, forming gas and biocrude. Biocrude are formed during HTC but mostly during HTL (15-23% for most feedstocks) with little during SCWG and none during TH. However increased temperature during SCWG produces the most gaseous products (30-33% for most feedstocks and 55% for microalgae).
- Aqueous products contain significant quantities of essential plant nutrients- N,P,K. Aqueous products from lower temperatures contain higher phosphorus levels (mainly organic-P and less phosphate) and lower nitrogen levels (mainly organic-N and less NH_3-N) while it is vice versa at high processing temperatures.
- Microalgae and chicken manure released P more easily (40-43%) than swine manure and digestate (9-14%) at the lowest temperature- thermal hydrolysis. Although the levels of extracted P depends on the presence of inorganics such as Ca, Mg and Fe in the feedstock processed. At higher temperatures, P is immobilised in solid product and precipitated as phosphate salts.
- Higher TOC are present in aqueous products from lower temperatures and decrease with increasing temperature. Therefore aqueous products from either TH, HTC or HTL could be used as feedstock into the SCWG process for syngas production.

Objective 2:

- Aqueous product from both thermal hydrolysis and HTC contain significant amounts of nutrients- N and P. Under neutral or alkali conditions, the recovered aqueous pH is acidic. Reduction in pH is increased with increasing temperature. Under acidic conditions, the recovered aqueous pH is increased.
- Aqueous products from thermal hydrolysis and HTC contain significant levels of organic-N and organic-P.
- Nitrogen extraction into the aqueous product is significantly affected by temperature rather than pH. Highest TN are extracted between 170-200°C and remains constant afterwards.
- NH_3-N extracted increases with increasing temperature and is affected by pH, highest levels achieved with mineral acid and lowest level with alkali.

- After low temperature hydrothermal processing, all aqueous products contain high organic-N (60-70%). Organic-N is highest between 170-200°C and then reduces with increasing temperature.
- Generally phosphorus extraction is pH and temperature dependent. Extraction of phosphorus reduces with increasing process temperature. Acidic conditions favour higher phosphorus extraction particularly with the addition of a mineral acid (H_2SO_4) at all temperatures and presents an opportunity for nutrient recovery.
- Neutral or basic conditions immobilizes phosphorus in the hydrochar and offers a potential route for manure management by reducing phosphorus loss to the environment. However the phosphorus may not be very bio-available.
- At higher temperatures (200-250°C), phosphorus in the aqueous product is readily available as inorganic-P (phosphate) with less than 3% organic-P for most additives but significant quantities of organic-P present using NaOH. Generally organic-P fraction in the aqueous product reduces under acidic conditions especially with H_2SO_4.
- After thermal hydrolysis at 120°C, the solid products contain 61-74% N for all additives and 63-84% P for most additives, extracting 11-30% into the aqueous

products. Mineral treatment with H_2SO_4 results in higher P extraction (79%) and about 11% P in the solid product.

- After thermal hydrolysis at 170°C, N is equally distributed between the solid and aqueous products using all additives while P is retained mostly in the solid (77-92%) for most additives except with mineral additive which extracted 94% P into the aqueous product, retaining 6% in the solid.
- During HTC 200-250°C, N is equally distributed between the solid and aqueous products while 86-98% and 91-98% P is retained in solid product using most additives at 200°C and 250°C respectively. Higher P extraction (80%) with H_2SO_4 at 200°C.
- Na and K were completely extracted into the aqueous products at the lowest temperature (120°C) and this was certainly the case at higher temperatures. Mg extraction into the aqueous product peaks at 170°C, and afterwards reduces with increasing temperature from 200-250°C.
- Ca extraction into the aqueous product is enhanced at lower pH. Acidic reagents extracted more Ca than neutral or alkali reagents. Although higher extractions with H_2SO_4 as organic acids had similar performance.
- Overall, Mg, Na and K were mostly present in the aqueous product while Ca, P was mainly in the solid product. Ca concentrates in the solid product as temperature increases from 120-250°C.
- Using additives, most micronutrients were mainly in the solid product except for Mn and Zn which were mostly extracted into the aqueous product using H_2SO_4. Extraction of Mn and Zn with H_2SO_4 peaks at 200°C, and concentrates in the solid at higher temperature (250°C). Generally, higher levels of micronutrients were extracted with acidic reagents compared to water or NaOH. Extraction of Mn and Zn with organic acids is similar.
- Increasing temperature from 120-250°C, did not increase the levels of Fe, Co, Cu. For Mn, increase in temperature increased its levels in the solid product especially for acidic reagents, but reduced in neutral or alkali conditions.
- During thermal hydrolysis, very low Al (<6%) in aqueous product for most additives. Al mainly in the solid product. Ni levels were also very low (<8%) in

the aqueous products from most additives, although with acetic acid significant extraction was observed. Generally Ni was more in the solid product. For instance with acetic acid, it was 67%. Pb extraction was <20% in the aqueous product for all additives although higher levels under neutral and alkali conditions. Increasing temperature to 170°C, increased Pb extraction; 25-33% under neutral and alkali conditions and 41% with H_2SO_4 and 31-33% with organic acids. Generally during thermal hydrolysis, Pb was mainly retained in the solid products for all additives.

- During HTC, very low Ni extractions into the aqueous product as well. In solid, low levels of Ni were observed (21-33%). At 200°C, also very low Al extractions (<7%) for most additives. Increase in temperature to 250°C reduced Al extractions. Generally Al is mainly in the solid product (67-78%) for most additives, but completely retained with NaOH. During HTC, Al is mainly associated with the solid product than the aqueous product. The presence of Pb in the aqueous product is more significant than Al or Ni. Higher Pb extractions with acidic reagents while Pb extraction reduced with increase in temperature to 250°C. Generally Pb is associated more with the solid products at higher temperatures; 68-82% for most additives and 48-64% with H_2SO_4.
- Energy content of hydrochar increase with process temperature and particularly higher under acidic conditions thus they could be used as fuel.

Objective 3:

- Significant levels of nitrogen and phosphorus are present in the aqueous product recovered after microwave pre-treatment under normal conditions with water.
- Nitrogen in the aqueous product was mainly in the form organic-N than NH_3-N for all feedstocks investigated while phosphorus in the aqueous product was mainly in the form of organic-P with sewage sludge and digestate, but occurred mainly as phosphate with microalgae and manures.
- Aqueous products from microwave pre-treatment contain nearly most of the potassium and sodium present in the unprocessed feedstock. Higher potassium

was extracted with microalgae and manures but not with sewage sludge and digestate.

- The microwave residues contain mainly calcium, magnesium and phosphorus for most feedstocks. Under normal conditions with water, microelements are mostly concentrated in the residue than the aqueous product.

Objective 4:

- Significant levels of nitrogen and phosphorus are present in the aqueous product recovered after microwave pre-treatment using additives.
- Higher TN extraction was achieved with water, alkali and mineral acid rather than the organic acids while higher TP extraction was achieved with the acidic reagents rather than water or NaOH.
- Using most additives, nitrogen in the aqueous product was mainly in the form of organic-N than NH_3-N except for acetic acid which had equal levels of these forms of nitrogen while phosphorus was present in the aqueous product as phosphate rather than organic-P except with NaOH which had equal distribution of these forms.
- Acidic conditions favour extraction of macro elements such as Ca, Mg, P and micro elements such as Co, Mn and Zn unlike neutral or alkaline conditions which extracted less of these elements making them concentrated in their residues. In particular with H_2SO_4, the highest levels of Fe, Co, Mn and Zn were extracted.

Objective 5:

- Generally microwave heating extracted more nitrogen into the aqueous product than conventional heating. Microwave heating also slightly increased phosphorus extraction when compared to conventional heating for most additives. However the type of heating did not affect the levels of phosphorus extracted using de-ionised water.

Objective 6:

- During cultivation trials, *Chlorella vulgaris* showed significant growth except for the aqueous product from SCWG of *Chlorella* at 1:50 dilution which may be attributed to inhibitory effect of nickel, phenols and fatty acids.

- *Chlorella* was able to utilise ammonium in the aqueous products as a source of nitrogen. At higher dilutions 1:400, there were insufficient nutrients in the culture media to promote growth.

- Overall, the biomass obtained from 1:50 dilution of catalysed SCWG of *S.latissima*, *L.digitata*, sewage sludge and 1:200 *Chlorella* were comparable with the biomass obtained with the standard Bold Basal Media. The recovered biomass could be used for biodiesel production or for lipid extraction.

Objective 7:

- Adsorption of phosphate is significantly affected by concentration as higher removal efficiencies were observed at lower concentrations. In this case the highest removal efficiencies were observed with 250mg/L phosphate.

- As typical concentrations of phosphate in the aqueous product from hydrothermal treatment of swine manure is many folds higher than threshold concentration, adsorption with biochar should be a secondary stage phosphate recovery method. It is suggested that these liquid waste streams from (TH or HTC) should be used as feedstock in HTL or SCWG and subsequently adsorption of phosphate from the aqueous product obtained after the process is feasible.

- Higher adsorption was achieved at higher pH of 8 and 9 compared to pH 7 forming more calcium phosphate in the adsorbed biochars as the pH increases. Consequently, there is no adsorption of phosphate at lower pH (acidic) conditions. There is no likelihood of struvite formation as traces of nitrogen were not detected while the composition of Mg remained constant in all the adsorbed biochars. However further investigation with XRD is needed to confirm this.

- Overall, the results on phosphorus recovery by adsorption suggests that this technique could be integrated with mineral acid hydrothermal processing and could be adapted in manure management.

9.3 Significance of results for process development

The overall aim of this research is to maximise extraction and recovery of vital plant nutrients especially phosphorus from wet wastes. The results presented indicate different recovery routes for nitrogen and phosphorus. Readily available forms of phosphorus (phosphate) and nitrogen (ammonium) are present in aqueous waste streams from hydrothermal processing. However maximum extraction of these nutrients are only evident in certain routes. While phosphorus is mostly recovered in the aqueous product from thermal hydrolysis at 170°C, it is mainly extracted as organic-P rather than phosphate. However with mineral acid such as H_2SO_4, 94% total phosphorus with 89% phosphate. This condition is ideal route for maximum P-recovery. On the other hand, nitrogen is mostly extracted at higher temperatures (HTL and SCWG) unlike phosphorus. In this study HTL was conducted at 350°C while SCWG was conducted at 500°C when most of the nitrogen in the feedstock is converted to ammonium with little organic-N remaining in the aqueous product. As a result, maximum recovery of nitrogen as ammonium is preferably by biological route by cultivating algal biomass. The biomass could be fed back into hydrothermal processing either the TH, HTC, HTL or SCWG routes generating pre-treated biomass for anaerobic digestion, biochar, biocrude or syngas respectively for biofuel production. The biomass could also be used for biodiesel production or as a source of useful chemicals.

As high phosphate aqueous waste streams (recovered from acid extractions) are considered for P-recovery by precipitation, lower phosphate aqueous waste streams from other additives especially at low processing temperatures may be considered as feed for SCWG process for syngas production as they are high in organic carbon as well. For the same reason, aqueous waste streams from TH, HTC and HTL may also be considered for SCWG process. CO_2 generated during HTL and HTC could be recycled to enhance algal growth during cultivation. Although SCWG, produces very small amounts of residue, it is rich in phosphorus. P-recovery from SCWG residues is possible after extraction of P in the solid with acid. It is suggested that P-recovery from aqueous waste streams should be by precipitation rather than adsorption as adsorption is significantly affected by concentration. For instance the concentration of phosphate from thermal hydrolysis of manure with mineral acid is typically high (usually in thousands). Whereas adsorption results indicate tolerable concentration of about 250mg/L which implies significant dilution before adsorption.

Extracting phosphorus using mineral acid leaves the hydrochar with the least phosphorus content. During HTC at 250°C, P-extraction from swine manure with mineral acid produced hydrochar with high energy value (28.5 MJ kg^{-1}) compared to the unprocessed swine manure (19.2 MJ kg^{-1}) which makes this hydrochar a valuable fuel source. At 170°C with mineral acid, which is the ideal route for maximum P-extraction, the hydrochar produced had higher energy content (22.4 MJ kg^{-1}) as well. The residues with higher P retention from HTC treatment under normal conditions with water and NaOH are useful as a soil improver. However the phosphorus may not be bio-available.

Finally, comparing microwave heating at 120°C for 15 minutes (**MH**) with conventional heating 120°C for 60 minutes (**CH**), nitrogen extraction is higher with MW than CH especially with H_2SO_4 and NaOH. Also with MW, P extraction increases with H_2SO_4 (4%). It also enhances formic acid and acetic acid P-extraction performance by 17% and 7% respectively. With these acids, about 80-90% phosphate is present in the aqueous product from MW. Considering the nutrient extraction benefits and shorter residence time, MW processing may also be considered for N and P recovery.

The overall integrated approach for by-product utilisation and potential nutrient recovery routes is proposed as shown in **Figure 9-1**.

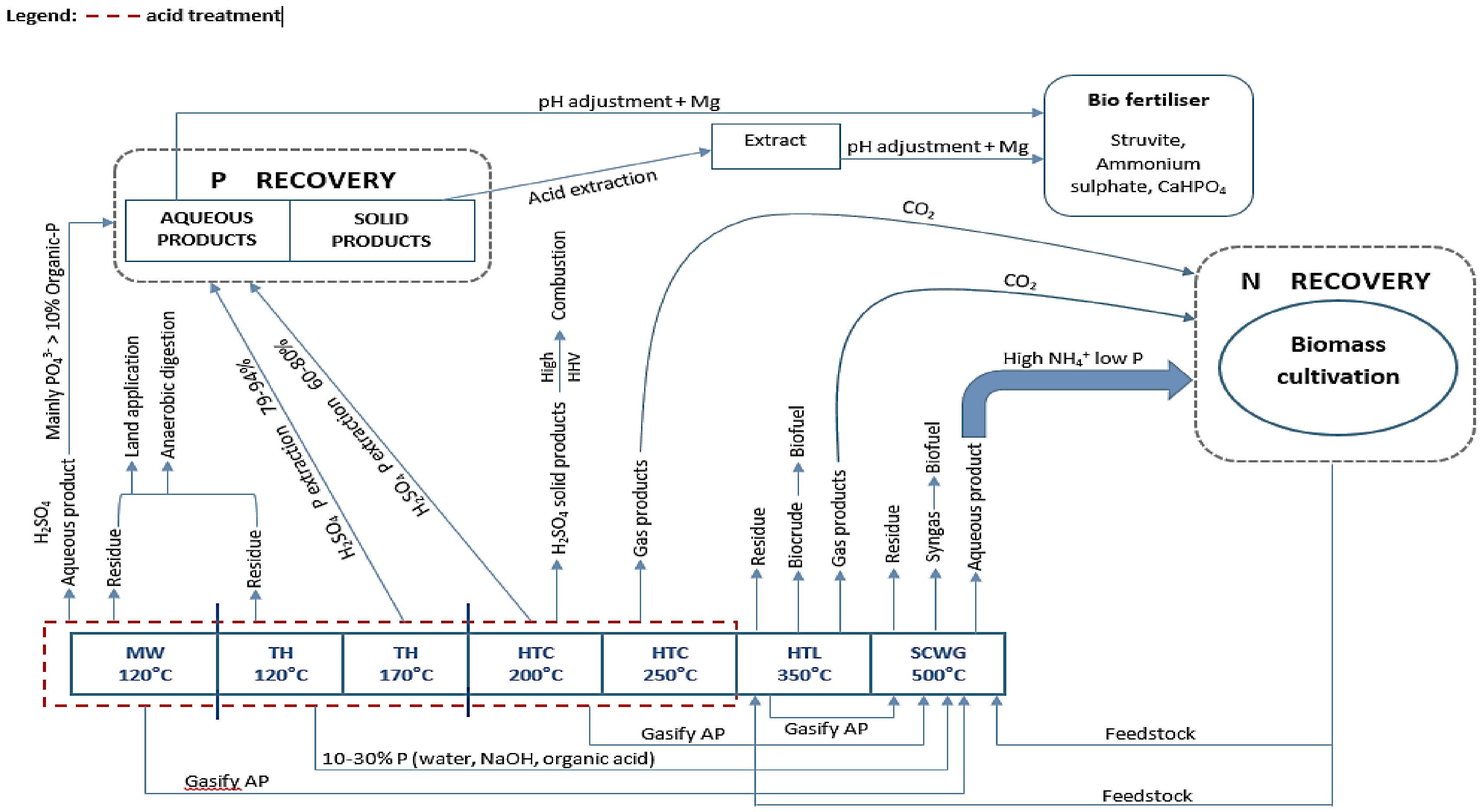


Figure 9-1: An Integrated approach for by-product utilisation and potential nutrient recovery routes

9.4 Future studies

Based on these findings, the following recommendations for future work are as follows:

- **Characterisation of aqueous products**

Aqueous products recovered during thermal hydrolysis, HTC, HTL and SCWG of *Chlorella vulgaris*, digestate, chicken manure and swine manure under normal conditions with water (**Objective 1**) may be further investigated with HPLC to determine the composition of biomolecules. Also the aqueous products from hydrothermal processing of swine manure with additives (**Objective 2**) may also be investigated with HPLC.

- **Improving nutrient extraction**

The results show that during hydrothermal processing of swine manure between 120°C-250°C, higher phosphorus extraction was achieved using 0.1M mineral acid (H_2SO_4) compared to the organic acids – Formic and acetic acid at the same concentration. Hydrothermal processing of swine manure at the same temperature range with increasing concentrations of the organic acids may be investigated. Concentrations from 0.2M to 0.5M is suggested to investigate the possibility of extracting more phosphorus into solution.

- **Biological recovery of nutrients**

Biological recovery of nutrients in HTC aqueous products using feedstocks such as sewage sludge, chicken manure, swine manure, *L.digitata*, *Chlorella vulgaris* in order to determine the inhibition effect on the growth of *Chlorella* and the most favourable dilution to obtain a higher biomass. Cultivation trials conducted in this research was with *Chlorella* is a fresh water algae, however other species of microalgae such as Dunaliella –a salt-water strain could be used as well. Other microorganisms such as yeast and bacteria could also be used. The effect of autotrophic, mixotrophic or heterotrophic growth of these microorganisms using HTC aqueous waste streams may be investigated.

- **Physical recovery of nutrients by adsorption**

Due to time constraints, optimum conditions such as pH, concentration, mixing etc were not performed during the adsorption experiments. Oak derived Mg-treated biochar was used for adsorption, however the effect of other types of biochar or support materials on phosphate removal efficiency should be investigated. The effect of pre-treating biochar with Fe or other metals salts on phosphate removal efficiency may also be investigated and compared with biochar pre-treated with Mg. The aqueous waste stream used for adsorption tests were from thermal hydrolysis and HTC of swine manure with H_2SO_4. Adsorption tests should be performed using aqueous waste stream from thermal hydrolysis and HTC of other feedstocks with H_2SO_4. These feedstocks may include chicken manure, sewage sludge, digestate and *Chlorella*. The properties of the adsorbed chars such as pore structure, surface area, energy density and the surface functionality groups may be investigated. The adsorbed chars may be analysed using XRD to determine the purity of the phosphate compound formed.

- **Physical recovery of nutrients by precipitation**

As waste streams from thermal hydrolysis and HTC contain significant quantities of ammonium and phosphorus, precipitation of struvite from these aqueous products may be performed by optimising conditions such as temperature, pH etc. The precipitate may be analysed further quantitatively and qualitatively to determine its purity.

Although during biological recovery, nitrogen was mainly utilised by microalgae in the form of ammonium present in the aqueous products. Nitrogen can also be recovered by precipitation. Recovery of nitrogen by precipitating ammonium sulphate should be performed with subsequent analysis of the precipitate by XRD to determine the purity. This is important to evaluate the feasibility of both thermal hydrolysis and HTC technology.

- **Other phosphate recovery methods**

The use of membrane technologies may be employed as a separation technique for large scale nutrient recovery from hydrothermal aqueous waste streams.

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APPENDIX 1

Table 0-1: Elemental composition of pure standard compounds

		N %	C %	H %	S %	O %
BBOT	$C_{26}H_{26}N_2O_2S$	6.48	72.36	6.11	7.44	7.45
dl-Methionine	$C_5H_{11}NO_2S$	9.39	40.25	7.43	21.49	21.45
Cystine	$C_6H_{12}N_2O_4S_2$	11.61	29.95	5.1	26.68	26.67
Sulphanilamide	$NH_2C_6H_4SO_2NH_2$	16.23	41.79	4.62	18.62	18.74
Atrophine	$C_{17}H_{23}O_3N$	4.84	70.56	8.01	0	16.59
Oatmeal		High				
Coal			High			

APPENDIX 2

Table 0-2: Metals leached into the aqueous product during thermal hydrolysis

Biomass	Concentration (mg kg^{-1})											
	K	Ca	Mg	Na	Fe	Al	Ni	Co	Cu	Pb	Mn	Zn
HTC 120°C												
water	11,990	1,710	4,570	3,090	30	0.3	0.05	0.17	0.9	0.5	10	70
0.1M NaOH	8,770	290	880	16,440	50	1.9	0.92	0.12	19.3	0.4	10	90
0.1M H_2SO_4	11,600	nd	8,530	3,000	90	3.9	2.26	0.26	0.5	0.4	290	380
0.1M Formic acid	12,340	6,170	7,130	3,160	30	0.3	1.11	0.20	1.0	0.3	80	190
0.1M Acetic acid	11,690	4,850	6,590	2,990	20	0.3	0.29	0.17	0.6	0.3	60	130
HTC 170°C												
water	12,680	2,180	6,090	3,220	140	2.2	-0.95	0.24	0.8	0.8	40	150
0.1M NaOH	11,220	670	2,660	21,660	120	1.7	0.75	0.18	13.8	0.6	8	80
0.1M H_2SO_4	13,140	12,430	9,350	3,430	290	23.4	0.97	0.39	1.1	1.0	330	490
0.1M Formic acid	13,060	5,680	7,560	3,290	260	4.0	-0.65	0.30	0.8	0.8	110	250
0.1M Acetic acid	12,910	5,680	7,310	3,280	200	2.8	6.88	0.30	0.7	0.8	100	200

nd Not determined

Table 0-3: Metals retained in the solid product during thermal hydrolysis

	Concentration (mg kg^{-1})											
Biomass	**K**	**Ca**	**Mg**	**Na**	**Fe**	**Al**	**Ni**	**Co**	**Cu**	**Pb**	**Mn**	**Zn**
Hyd 120°C												
water	1,310	32,740	5,720	260	1,130	410	7	0.7	170	4.4	400	690
0.1M NaOH	4,400	35,250	9,310	7,430	1,140	390	6	0.8	140	2.0	400	650
0.1M H_2SO_4	1,330	18,820	1,130	340	500	470	8	0.5	190	2.0	60	280
0.1M Formic acid	940	29,270	3,060	230	1,070	410	6	0.8	180	2.2	340	560
0.1M Acetic acid	1,770	29,608	3,510	390	1,080	790	6	0.5	219	1.9	350	620
Hyd 170°C												
water	970	41,510	5,190	260	1,320	510	9	0.9	220	2.8	470	820
0.1M NaOH	2,810	46,190	9,960	4,530	1,330	500	8	0.9	200	2.7	560	920
0.1M H_2SO_4	530	28,060	770	140	560	550	9	0.4	250	1.9	40	240
0.1M Formic acid	470	39,550	3,430	160	1,180	560	9	0.7	240	3.0	410	670
0.1M Acetic acid	460	40,150	3,810	160	1,280	540	30	0.7	250	3.0	430	760

Table 0-4: Metals leached into the aqueous product during HTC

	Concentration (mg kg^{-1})											
Biomass	**K**	**Ca**	**Mg**	**Na**	**Fe**	**Al**	**Ni**	**Co**	**Cu**	**Pb**	**Mn**	**Zn**
HTC 200°C												
water	13,120	1,600	6,300	3,270	140	2.4	-2.02	0.24	0.5	0.9	50	130
0.1M NaOH	12,640	1,110	5,230	23,660	130	2.3	-0.39	0.23	0.8	0.7	30	70
0.1M H_2SO_4	13,120	12,030	8,200	3,380	310	33.1	1.29	0.37	0.6	1.3	270	440
0.1M Formic acid	13,320	3,410	7,300	3,320	220	5.0	-1.40	0.28	0.4	0.9	80	210
0.1M Acetic acid	13,570	2,950	7,000	3,420	190	3.5	-1.77	0.28	0.4	0.9	70	180
HTC 250°C												
water	13,340	1,780	5,400	3,350	6	0.3	-3.37	0.09	0.1	0.9	30	10
0.1M NaOH	13,500	1,020	3,160	25,210	1	0.2	-0.08	0.08	0.2	0.2	10	10
0.1M H_2SO_4	13,590	11,800	5,140	3,410	120	18.5	-3.97	0.25	0.3	1.1	160	190
0.1M Formic acid	13,350	1,860	6,110	3,320	10	0.6	-2.72	0.09	0.1	0.8	30	10
0.1M Acetic acid	13,300	2,690	6,320	3,360	30	1.0	-3.87	0.10	0.1	1.0	50	20

Table 0-5: Metals retained in the solid product during HTC

Biomass	Concentration (mg kg^{-1})											
	K	**Ca**	**Mg**	**Na**	**Fe**	**Al**	**Ni**	**Co**	**Cu**	**Pb**	**Mn**	**Zn**
HTC 200°C												
water	440	48,130	5,620	160	1,360	600	10	1.3	250	3.1	520	1,030
0.1M NaOH	1,470	50,360	6,990	2,590	1,460	770	10	0.8	260	3.3	570	1,020
0.1M H_2SO_4	880	29,710	2,710	220	690	540	10	0.6	250	2.0	150	330
0.1M Formic acid	520	45,040	4,160	180	1,170	580	10	0.7	250	2.8	480	750
0.1M Acetic acid	370	46,590	4,780	140	1,360	620	10	0.8	250	2.8	500	830
HTC 250°C												
water	380	64,070	9,010	130	2,010	790	20	1.1	330	4.4	730	1,450
0.1M NaOH	420	64,410	12,460	810	2,060	810	20	1.1	320	4.6	730	1,380
0.1M H_2SO_4	380	36,100	8,770	150	1,480	680	20	1.0	310	3.2	420	980
0.1M Formic acid	330	63,430	7,590	160	1,990	860	10	1.1	330	4.4	730	1,430
0.1M Acetic acid	280	63,770	7,300	130	2,000	880	20	1.2	330	4.0	710	1,450

APPENDIX 3

Table 0-6: Turbidity and pH data from cultivation trials using SCWG catalysed aqueous product

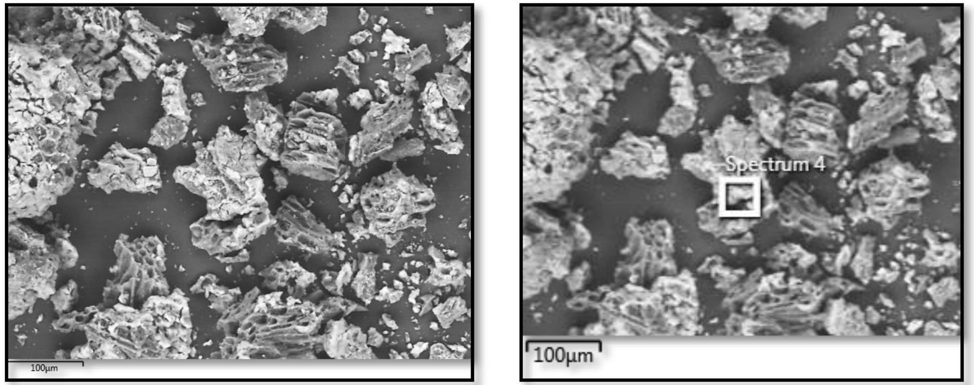
Control Media					**C 1:50**					**C 1:200**					**C 1:400**				
Log T	Log T	Mean	Mean pH	STDEV	Log T	Log T	Mean	Mean pH	STDEV	Log T	Log T	Mean	Mean pH	STDEV	Log T	Log T	Mean	Mean pH	STDEV
1.78	2.34	2.06	6.9	0.40	1.77	2.33	2.05	8.3	0.39	1.75	2.31	2.03	8.7	0.40	1.79	2.33	2.06	8.7	0.38
1.99	2.39	2.19	7.3	0.28	2.06	2.43	2.25	9.0	0.26	2.03	2.35	2.19	9.3	0.22	2.01	2.36	2.19	9.2	0.25
2.19	2.47	2.33	7.8	0.20	2.30	2.50	2.40	9.5	0.14	2.23	2.41	2.32	8.8	0.13	2.20	2.40	2.30	8.6	0.14
2.34	2.52	2.43	8.2	0.12	2.43	2.56	2.50	9.9	0.09	2.30	2.43	2.36	9.0	0.10	2.24	2.42	2.33	8.6	0.13
2.45	2.54	2.50	8.5	0.07	2.50	2.60	2.55	9.7	0.07	2.34	2.45	2.40	8.7	0.07	2.29	2.43	2.36	8.2	0.10
2.57	2.66	2.62	9.5	0.07	2.56	2.64	2.60	9.2	0.05	2.37	2.47	2.42	8.5	0.07	2.33	2.46	2.39	8.3	0.09
2.66	2.72	2.69	10.1	0.04	2.59	2.66	2.62	9.6	0.06	2.38	2.48	2.43	8.2	0.08	2.33	2.46	2.40	8.0	0.09
2.76	2.77	2.76	10.4	0.01	2.61	2.68	2.65	9.6	0.05	2.41	2.50	2.45	8.3	0.06	2.37	2.47	2.42	8.1	0.08
2.83	2.81	2.82	10.5	0.01	2.64	2.70	2.67	9.6	0.04	2.44	2.53	2.48	8.4	0.07	2.39	2.50	2.45	8.0	0.08
2.85	2.86	2.86	10.5	0.01	2.65	2.72	2.68	9.8	0.05	2.45	2.54	2.50	8.6	0.06	2.41	2.52	2.46	8.3	0.08
2.95	2.90	2.93	10.7	0.04	2.66	2.71	2.68	9.7	0.03	2.46	2.53	2.50	8.4	0.05	2.41	2.52	2.47	8.5	0.07
3.04	2.94	2.99	10.9	0.07	2.66	2.72	2.69	9.8	0.04	2.47	2.54	2.50	8.5	0.05	2.42	2.53	2.47	8.4	0.08
3.07	2.98	3.02	10.7	0.06	2.67	2.75	2.71	9.8	0.05	2.49	2.54	2.51	8.3	0.04	2.43	2.54	2.49	8.2	0.08
3.12	3.01	3.06	10.7	0.08	2.68	2.75	2.72	9.4	0.05	2.50	2.58	2.54	8.0	0.05	2.46	2.54	2.50	8.0	0.06

Table 0-7: Turbidity and pH data from cultivation trials using SCWG non-catalysed aqueous product

Control Media					**NC 1:50**					**NC 1:200**					**NC 1:400**				
Log T	Log T	Mean	Mean pH	STDEV	Log T	Log T	Mean	Mean pH	STDEV	Log T	Log T	Mean	Mean pH	STDEV	Log T	Log T	Mean	Mean pH	STDEV
1.78	2.34	2.06	6.9	0.40	1.64	2.30	1.97	8.5	0.46	1.79	2.36	2.08	8.9	0.40	1.78	2.35	2.07	8.8	0.41
1.99	2.39	2.19	7.3	0.28	1.74	2.32	2.03	8.3	0.41	1.95	2.37	2.16	9.1	0.30	1.96	2.38	2.17	8.6	0.29
2.19	2.47	2.33	7.8	0.20	1.93	2.40	2.17	8.5	0.33	2.17	2.38	2.27	8.5	0.15	2.14	2.37	2.25	8.5	0.17
2.34	2.52	2.43	8.2	0.12	2.15	2.44	2.30	8.8	0.20	2.23	2.41	2.32	8.7	0.13	2.18	2.37	2.28	8.5	0.14
2.45	2.54	2.50	8.5	0.07	2.23	2.45	2.34	8.7	0.16	2.28	2.41	2.34	8.3	0.10	2.22	2.38	2.30	8.3	0.11
2.57	2.66	2.62	9.5	0.07	2.31	2.49	2.40	8.7	0.12	2.30	2.41	2.36	8.6	0.08	2.25	2.40	2.33	8.3	0.10
2.66	2.72	2.69	10.1	0.04	2.35	2.52	2.43	9.0	0.12	2.31	2.40	2.36	8.8	0.06	2.25	2.36	2.30	8.4	0.08
2.76	2.77	2.76	10.4	0.01	2.38	2.53	2.45	9.0	0.11	2.33	2.43	2.38	8.9	0.07	2.28	2.41	2.35	8.4	0.09
2.83	2.81	2.82	10.5	0.01	2.41	2.57	2.49	8.9	0.12	2.37	2.45	2.41	8.6	0.06	2.32	2.44	2.38	8.5	0.09
2.85	2.86	2.86	10.5	0.01	2.41	2.59	2.50	9.1	0.12	2.38	2.46	2.42	8.6	0.06	2.34	2.42	2.38	8.6	0.05
2.95	2.90	2.93	10.7	0.04	2.43	2.52	2.47	9.0	0.07	2.39	2.47	2.43	8.7	0.05	2.35	2.40	2.38	8.4	0.04
3.04	2.94	2.99	10.9	0.07	2.44	2.59	2.51	9.1	0.11	2.39	2.47	2.43	8.7	0.06	2.35	2.40	2.37	8.5	0.03
3.07	2.98	3.02	10.7	0.06	2.40	2.63	2.51	9.2	0.16	2.41	2.48	2.44	8.4	0.05	2.34	2.43	2.38	8.4	0.06
3.12	3.01	3.06	10.7	0.08	2.46	2.64	2.55	9.1	0.13	2.43	2.48	2.46	8.2	0.04	2.37	2.37	2.37	8.4	0.00

Table 0-8: Turbidity and pH data from cultivation trials using SCWG aqueous products from *Chlorella*, *L.digitata* and sewage sludge

Control Media		***Chlorella***						**L.digitata**						**Sewage sludge**					
		1:50		1:200		1:400		1:50		1:200		1:400		1:50		1:200		1:400	
Log T	pH	Log T	pH	Log T	pH	Log T	pH	Log T	pH	Log T	pH	Log T	pH	Log T	pH	Log T	pH	Log T	pH
1.54	6.63	1.8	8.54	1.63	8.49	1.7	8.61	1.9	7.47	1.66	8.78	1.6	9.17	1.8	8.45	1.70	8.96	1.62	9.05
1.74	6.65	1.8	8.52	1.85	8.67	1.9	9.06	2.0	7.75	1.89	8.94	1.8	8.86	2.0	8.39	1.97	8.68	1.93	9.13
1.76	6.85	2.0	8.40	2.08	9.07	2.1	9.31	2.0	8.61	2.00	9.54	1.9	9.18	2.1	8.44	2.14	9.20	2.04	9.36
1.75	6.90	1.8	8.55	2.16	9.52	2.2	9.59	2.1	9.86	2.07	9.91	2.0	9.14	2.1	8.74	2.26	9.72	2.15	9.55
1.87	7.06	1.8	8.62	2.17	9.54	2.2	9.34	2.1	9.52	2.11	9.81	2.0	9.43	2.1	8.92	2.29	9.46	2.17	9.41
2.01	7.12	1.9	8.66	2.23	9.06	2.3	8.93	2.3	9.79	2.14	9.62	2.1	8.59	2.2	9.01	2.37	9.15	2.20	9.29
2.13	7.19	1.9	8.61	2.18	8.91	2.3	8.36	2.3	9.31	2.14	9.15	2.1	8.51	2.3	9.01	2.40	9.07	2.22	8.94
2.19	7.26	1.9	8.71	2.20	8.65	2.3	8.58	2.3	9.43	2.15	9.2	2.12	7.94	2.3	9.08	2.39	9	2.28	8.83
2.27	7.37	1.9	8.53	2.27	8.08	2.3	8.10	2.3	9.58	2.15	8.78	2.18	7.96	2.3	8.79	2.42	8.77	2.30	8.53
2.39	7.66	1.9	8.64	2.16	8.6	2.4	8.22	2.3	9.47	2.15	9.08	2.18	8.12	2.3	8.92	2.43	8.7	2.31	7.96
2.49	7.89	2.0	8.65	2.15	8.12	2.4	8.41	2.3	8.75	2.18	8.59	2.15	7.91	2.3	8.98	2.43	8.11	2.32	7.79
2.57	8.68	1.98	8.64	2.16	8.09	2.4	8.54	2.3	9.08	2.16	8.42	2.23	7.8	2.4	9.03	2.44	8.29	2.37	8.01
2.64	9.01	1.95	8.55	2.20	7.62	2.4	8.28	2.3	8.77	2.21	8.22	2.25	7.65	2.4	9.02	2.44	8.07	2.38	7.53
2.72	9.34	1.95	8.55	2.20	7.62	2.4	8.28	2.3	8.77	2.21	8.22	2.25	7.65	2.4	9.02	2.44	8.07	2.38	7.53



Element	Atomic %
C	63.21
O	28.46
Na	0.09
Mg	2.40
P	2.73
S	0.07
K	0.03
Ca	2.87
Fe	0.09
Zn	0.05
Total:	100.00

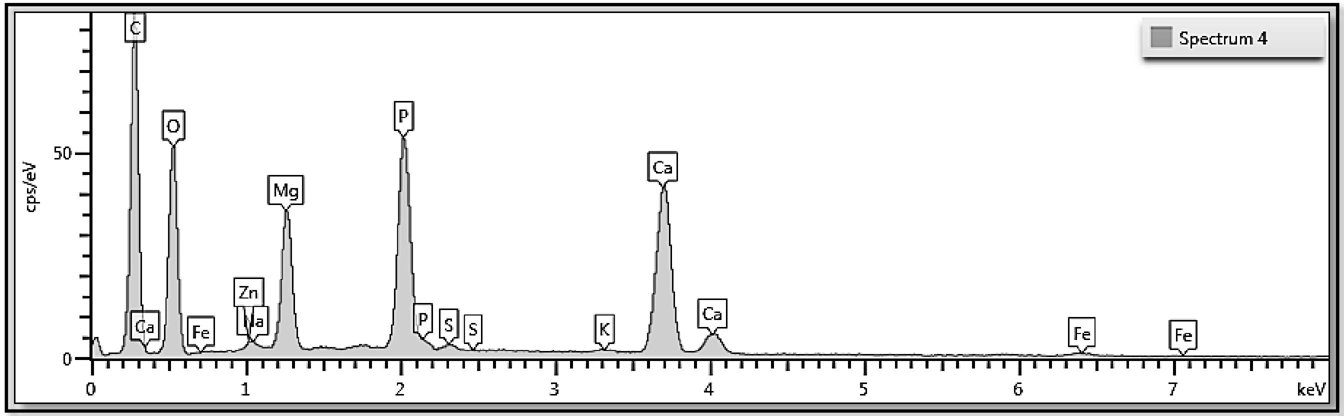
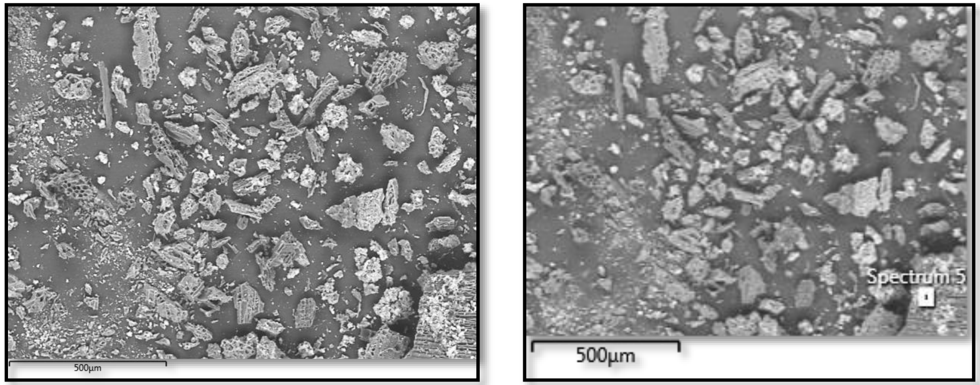


Figure 1: Adsorbed biochar from 120°C H_2SO_4 pH 7



Element	Atomic %
C	68.37
O	24.41
Na	0.11
Mg	1.64
P	2.44
Cl	0.03
K	0.02
Ca	2.76
Mn	0.05
Fe	0.16
Total:	100.00

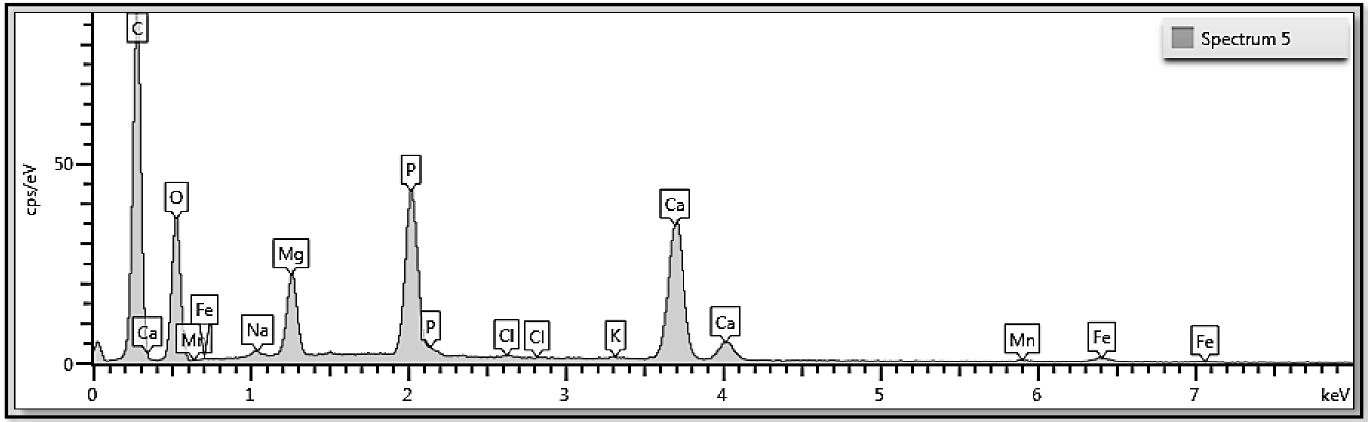
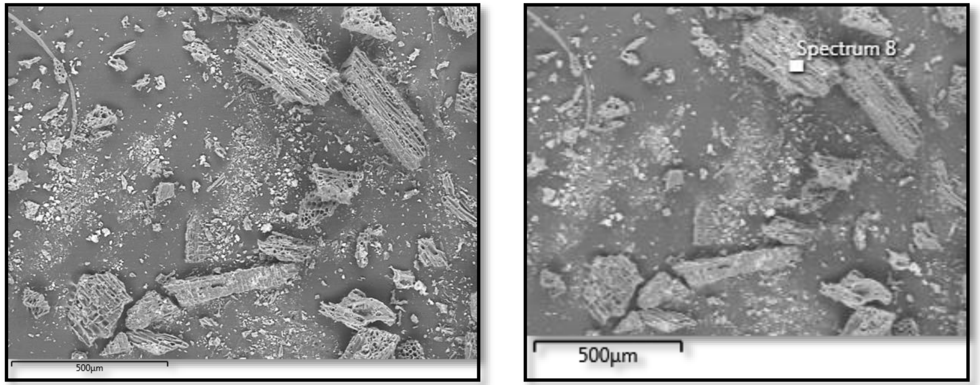


Figure 2: Adsorbed biochar from 170°C H_2SO_4 pH 7



Element	Atomic %
C	67.01
O	22.08
Na	0.24
Mg	1.93
Al	0.10
Si	0.28
P	3.36
S	0.08
Cl	0.03
K	0.05
Ca	4.39
Mn	0.07
Fe	0.20
Cu	0.07
Zn	0.12
Total:	100.00

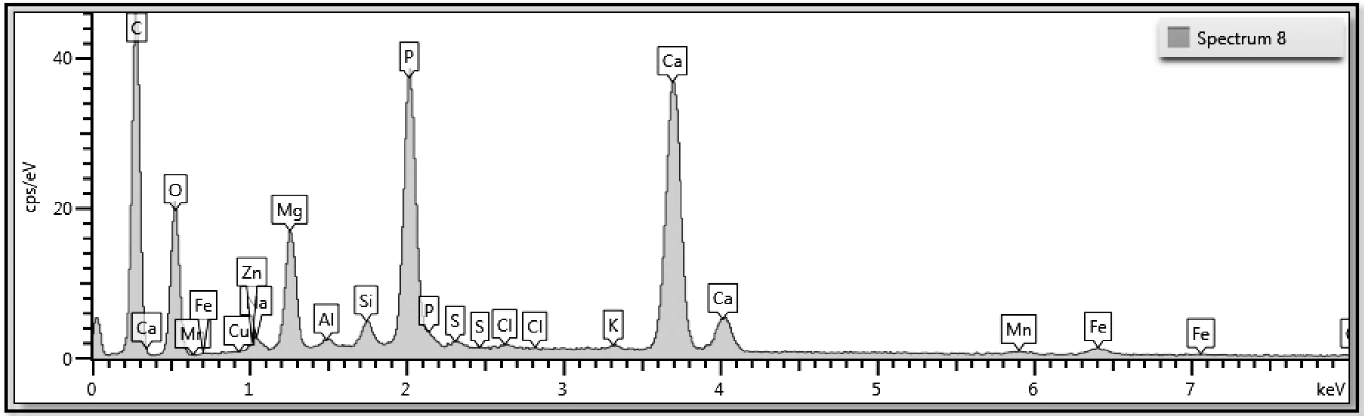
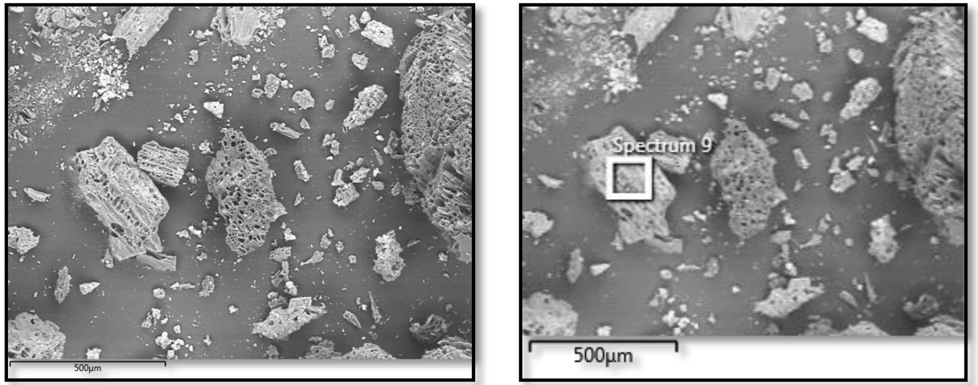


Figure 3: Adsorbed biochar from 200°C H_2SO_4 pH 7



Element	Atomic %
C	75.73
O	17.49
Na	0.07
Mg	4.28
P	1.00
Ca	1.38
Fe	0.04
Total:	100.00

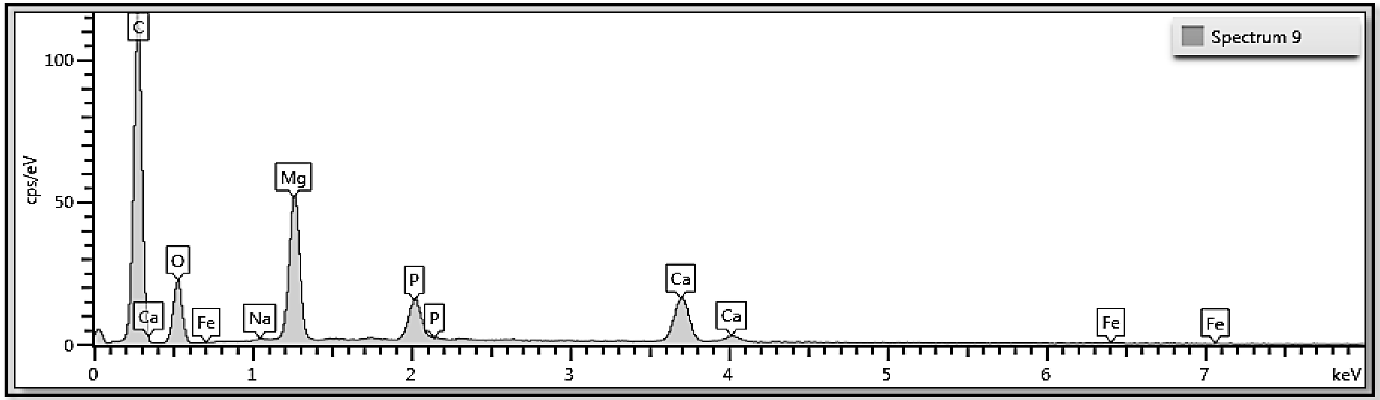
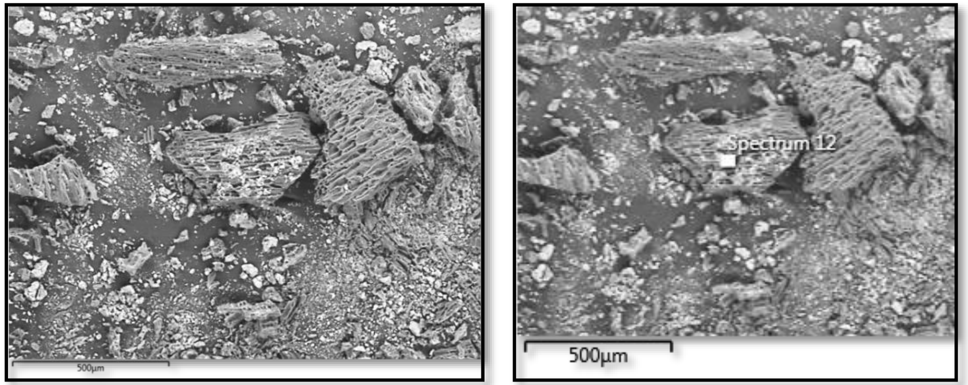


Figure 4: Adsorbed biochar from 250°C H_2SO_4 pH 7



Element	Atomic %
C	61.66
O	27.40
Na	0.13
Mg	1.66
P	3.86
S	0.07
K	0.04
Ca	5.05
Mn	0.05
Fe	0.07
Total:	100.00

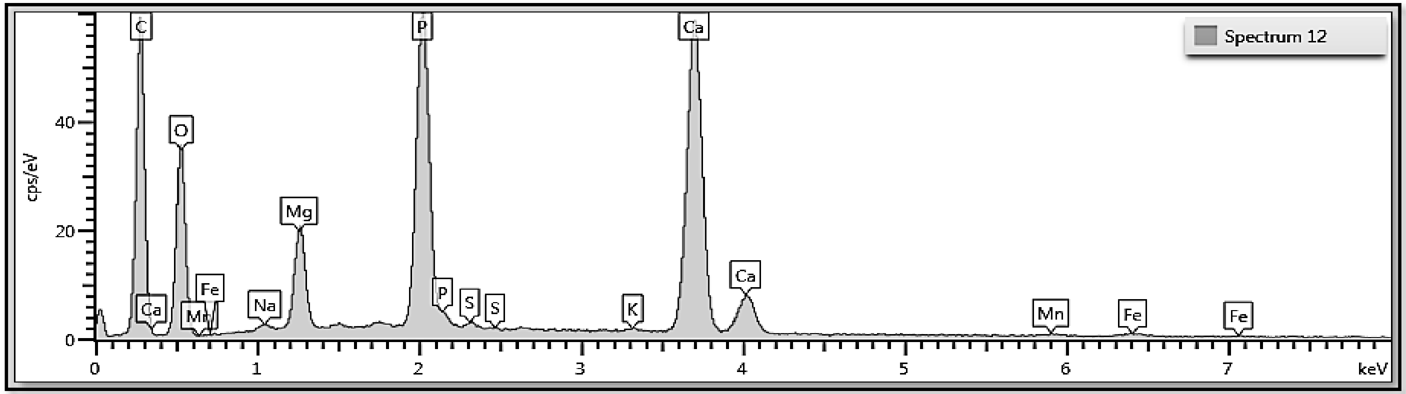
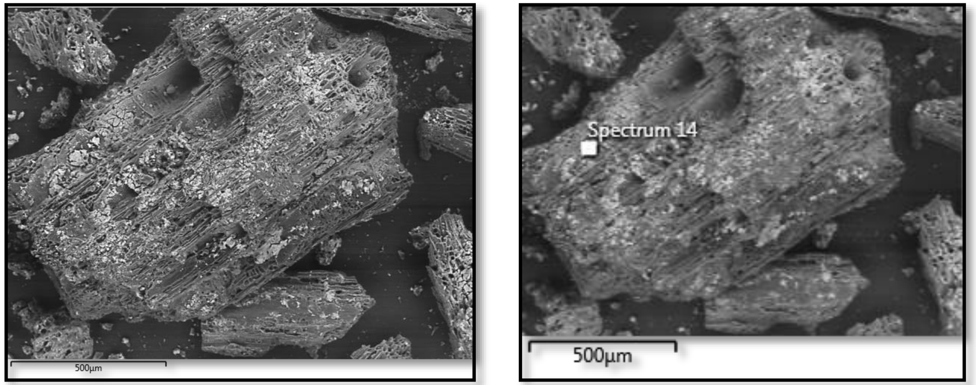


Figure 5: Adsorbed biochar from 250°C H_2SO_4 pH 8



Element	Atomic %
C	58.66
O	30.97
Na	0.12
Mg	3.57
P	3.09
K	0.03
Ca	3.50
Fe	0.07
Total:	100.00

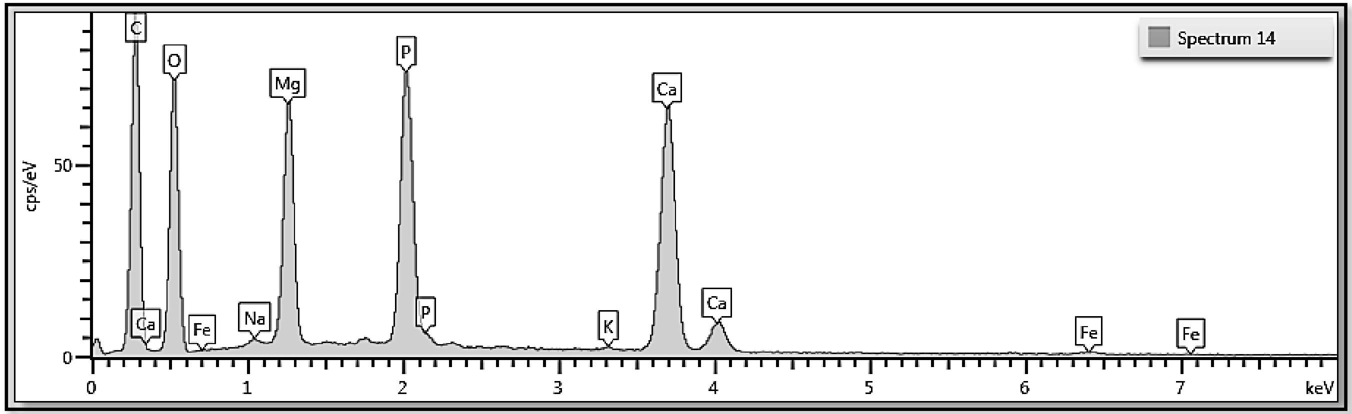
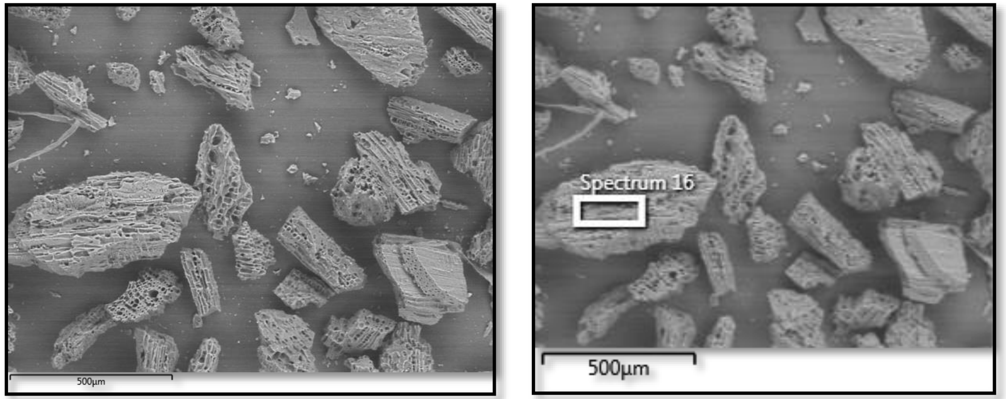


Figure 6: Adsorbed biochar from 250°C H_2SO_4 pH 9



Element	Atomic %
C	88.01
O	8.24
Mg	3.59
Cl	0.08
K	0.02
Ca	0.06
Total:	100.00

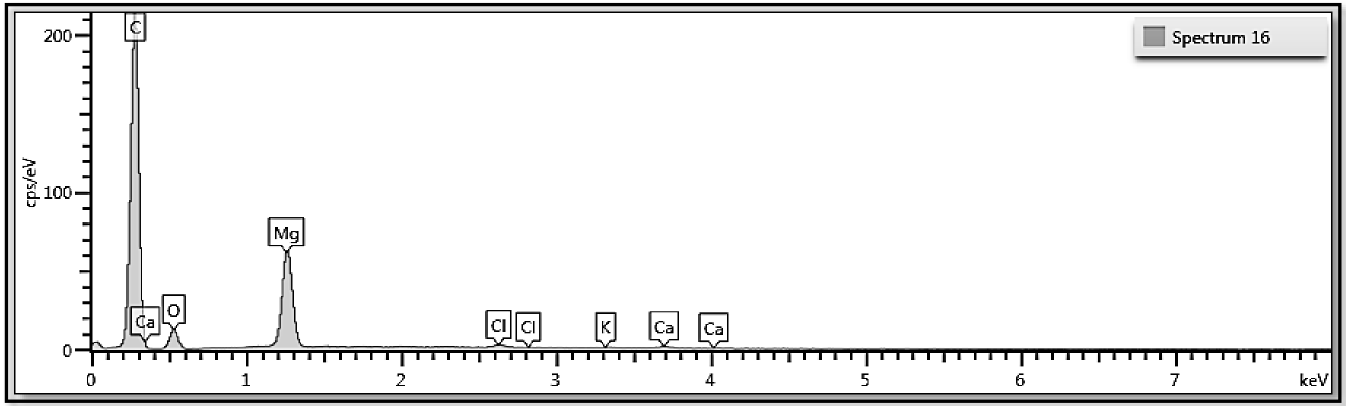


Figure 7: Adsorbed biochar from 250°C H_2SO_4 no pH adjustment