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A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate

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Thermal hydrolysis and hydrothermal processing have shown promise for converting biomass into higher energy density fuels. Both approaches can facilitate the extraction of inorganics in to the aqueous process waters. This study compares the behaviour of microalgae, digestate, swine and chicken manure by thermal hydrolysis and hydrothermal processing at increasing process severity. Thermal hydrolysis was performed at 170 °C, hydrothermal carbonization (HTC) was performed at 250 °C, hydrothermal liquefaction (HTL) was performed at 350 °C and supercritical water gasification (SCWG) was performed at 500 °C in a batch reactor. The level of nitrogen, phosphorus and potassium in the product streams was measured for each feedstock. Nitrogen is present in the aqueous phase as organic-N and NH_3-N. The proportion of organic N increases the lower the temperature. The extraction of phosphorus is strongly linked to the presence of inorganics such as Ca, Mg and Fe in the starting feedstock. Microalgae and chicken manure release phosphorus more easily than the other feedstocks.

Keywords: hydrothermal processing, NPK, manure, microalgae, digestate

1. Introduction

Hydrothermal processing of biomass can be utilised as either a pre-treatment or for energy densification. Thermal hydrolysis is often used prior to anaerobic digestion at temperatures in the range 160-170 °C resulting in enhanced biogas yields (Mendez et al., 2015). Hydrothermal carbonisation (HTC) is operated at 180-250 °C and pressure between 2-10 MPa, and produces a carbon-rich bio-coal (Mumme et al., 2011). Hydrothermal liquefaction (HTL) is operated at 280-370 °C and pressures ranging from 10-25 MPa and produces a synthetic bio-crude (Biller et al., 2012). Supercritical water gasification (SCWG) is operated at temperatures above 450 °C and pressure above the critical point of water (22 MPa) producing a syngas containing H_2, CO_2 and CH_4 (Toor et al., 2011). There is a growing interest in the recovery of nutrients from wet wastes such as manures and bio-solids and hydrothermal processing has been proposed to facilitate the extraction of nitrogen, phosphorus and potassium from these materials (Biller et al., 2012; Heilmann et al., 2014). Concentrated animal feeding operations (CAFOs) such as dairy, swine and poultry produce significant amounts of manure which pose challenges for safe and effective disposal. Manures from piggeries, poultry and dairy farming are commonly applied to land as fertilizers or are processed by anaerobic digestion following which digestate can be applied to land.

Extensive research has focussed on the hydrothermal processing of wastes such as sewage sludge (Melero et al., 2015; vom Eyser et al., 2015; 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; Theelaga and Midgett, 2012; Chen et al, 2014; Titirici et al., 2007; Funke and Ziegler, 2010; Berge et al., 2011; Lu et al., 2013). A number of studies have investigated the fate of phosphorus in either the solid product or the aqueous product. Heilmann et al., (2014) demonstrated that during the HTC of swine, diary and chicken manures, over 90% of the phosphorus was associated with the hydrochar precipitated as phosphate salts. Similarly, Dai et al., (2015), investigated the immobilisation of phosphorus (P) in hydrochar from diary manure at 200 °C and observed an increase in apatite P due to the high levels of calcium in the hydrochar. In this study, HTC was proposed as a method of manure management, reducing soluble P and reducing the risk of P loss to the environment. He et al., (2000) performed HTL of swine manure at temperatures between 275 and 350 °C and observed that the reaction conditions had little influence on the distribution of nitrogen, phosphorus and potassium species (NPK) which was mainly found in the aqueous product (He et al., 2000).

Hydrothermal liquefaction of microalgae have indicated that a large proportion of the nitrogen and the phosphorus in the feedstock are found in the aqueous phase (Yu et al., 2011; Yu et al., 2014), and highlighted that the fate of P is closely linked to the metal composition of the feedstock. Feedstock high in calcium or magnesium will favour precipitation of the P into the solid phase (Yu et al., 2014). This is in agreement with the immobilisation of P as described by Heilmann et al. (2014). A number of reports have shown that there are sufficient nutrients in the process waters following HTL and SCWG (Biller et al., 2012; Cherad et al., 2013; Lopez Barreiro et al., 2015; Tsukahara et al., 2001; Jena et al., 2011) and hydrothermal carbonisation of algae (Du et al., 2012) to cultivate fresh microalgae. Lopez Barreiro et al. (2014) observe that the levels of ammonium in the process waters increase following gasification compared to liquefaction. The levels of phosphate recovery in the process water were found to vary with feedstock (Lopez Barreiro et al., 2014) and once again are linked to the inorganic content of the feedstock.

Hydrothermal processing therefore has the potential for facilitating the recovery of nutrients although its extraction is feedstock dependent. To the authors' knowledge, no study has previously compared the extraction of NPK from the same feedstock via all four hydrothermal processing routes using the same reactor conditions. This study investigates the 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.

2. Experimental

2.1 Materials

The four biomass feedstocks used in this study were obtained from different sources. Chlorella vulgaris was obtained as a dry powder from a commercial source. The sewage sludge digestate was provided by OWS (Belgium). The poultry and swine manure were collected from the University of Leeds farm. The manure and the digestate were pre-dried in an oven at 60 °C for several days after which they were ground into powder using an Agate Tema barrel before characterization. The samples in powder form were used to produce slurries during the hydrothermal processing.

Ultimate analyses was performed using a CE Instruments Flash EA 1112 series elemental analyser to determine the percentage composition of carbon, hydrogen, nitrogen, sulphur and oxygen (CHNSO) of the dry unprocessed biomass samples. Proximate analyses were performed using a Thermogravimetric analyser (TGA) to determine the moisture, ash and volatile contents. Metal analysis of the feedstock was analysed following digestion of the samples in Nitric acid. Metals such as potassium, calcium, magnesium, sodium, iron and aluminium were analysed using atomic absorption spectroscopy (AAS), while nickel and cobalt were analysed using inductively coupled plasma mass spectrometry (ICP-MS). Phosphorus in the unprocessed biomass samples was determined by colorimetry using the ascorbic acid method. All measurements were performed in duplicate and the mean values have been reported. Total nitrogen present in each aqueous product was determined by the Kjedahl method (TKN) and ammonium by a distillation method followed by titration.

2.2 Hydrothermal processing

Hydrothermal treatment of each feedstock was conducted at different temperatures in a 75mL batch Parr reactor charged with a slurry containing 3 g of feedstock in 27 mL of de-ionized water. Hydrolysis was performed at 170 °C for 1 hour, hydrothermal carbonization was performed at 250 °C for 1 hour and hydrothermal liquefaction was performed at 350 °C for 1 hour. Finally gasification experiments were performed at 500 °C for 30 minutes using 1g of feedstock in 15 mL of de-ionised water. In each case the residence time was taken from the point the reactor reached the desired temperature. The heating rate was 10 ℃ min^{-1} and the cooling rate was in a similar range. The heating and cooling rates are the same for each feedstock as the same reactor was used for all the experiments. A more detailed description of the experimental set up is described elsewhere (Biller et al., 2012; Cherad et al., 2016).

2.3 Product recovery and analysis

Following hydrothermal treatment, the reactor was allowed to cool to room temperature before emptying. In the case of the gasification experiments, the gas is removed for further analysis. The solid residues and the aqueous products were separated by filtration using a pre-weighed Whatman filter paper. The remaining content in the reactor was rinsed with 10 ml of distilled water and filtered. The aqueous product was collected in a volumetric flask and made up to 50 ml with de-ionized water. All residues recovered were allowed to dry overnight at room temperature and weighed afterwards. Significant quantities of bio-crude were produced during the HTC and HTL process. As a result of this, the residue and reactor was rinsed with dichloromethane in order to extract the bio-crude. The weight of the bio-crude recovered from each process was obtained after evaporating the organic solvent following the methods described previously (Biller and Ross, 2011).

Analysis of the aqueous phase

The pH of the concentrated aqueous product was measured before dilution with makeup water. The concentration of total carbon (TC) and inorganic carbon (IC) in the recovered aqueous products were determined using a Shimadzu TOC-5000. The total organic carbon (TOC) concentration in each aqueous product is reported as the difference between TC and IC concentrations. Metals such as potassium, calcium, magnesium, sodium, iron and aluminium were analysed using atomic absorption spectroscopy (AAS) while nickel and cobalt were analysed using inductively coupled plasma mass spectrometry (ICP-MS).

Total phosphorus and reactive phosphorus concentrations in each of the aqueous product recovered were determined by colorimetry using the ascorbic acid method. The water phase requires a pre-digestion step using the persulphate digestion method before colorimetric analysis. After digestion, the samples were made up to a known volume (100 mL) The Total nitrogen present in each aqueous product was determined by the Kjedahl method. This involved acid digestion of an aliquot of sample (10 mL) with concentrated sulphuric acid together with the Kjedahl catalyst. After complete digestion (as indicated by a greenish colour) the samples were left to cool before the distillation step. Sample distillation into a 50 ml boric acid solution was followed by titration with 10 mM sulphuric acid to measure the released ammonia.

In the case of ammoniacal nitrogen (NH_3 -N) determination, known sample volumes were used directly in the distillation step, as no pre-digestion with acid is needed. The titration was performed as stated above.

Analysis of solid residue

About 10 mg of each recovered residue was analysed using a TA Instruments Q5000 thermo-gravimetric analyser to determine the percentage of moisture, volatiles and ash contents. The ultimate analysis (CHNSO content) of the residues was analysed using a CE Instruments Flash EA 1112 series elemental analyser. Oxygen was calculated by difference. Metals such as potassium, calcium, magnesium, sodium, iron and aluminium were analysed using atomic absorption spectroscopy (AAS) while nickel and cobalt were analysed using the inductively coupled plasma mass spectrometry (ICP-MS) following acid digestion in nitric acid. Phosphorus in the processed biomass samples was analysed by colorimetry using the ascorbic acid method. All measurements were performed in duplicate and the mean values are reported.

3. Results and Discussion

3.1 Characterisation of feedstock

The proximate and ultimate analyses of the four feedstock investigated are listed in **Table 1**. The results show that nitrogen content was highest for the microalgae (C.vulgaris) at 9.9 wt.% followed by the chicken manure (5.7 wt.%) and swine manure (3.1 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 proportion of ash in each feedstock was high. The swine manure, chicken manure and microalgae had similar levels of ash ranging from 10-11 wt.% while the digestate contained significantly higher ash levels (60 wt.%). The microalgae and manure contained the higher carbon and hydrogen content at 47 wt.% and 6-7 wt.% respectively. The carbon and hydrogen content in the chicken manure was lower. 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 wt.%). This reduction in carbon is due to the high levels of ash following anaerobic treatment. **Table 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 (8 MJ kg^{-1}) while the microalgae has the highest (22 MJ kg^{-1}). The swine and chicken manures were similar at 19 MJ kg^{-1} and 18MJ kg^{-1} respectively.

Table 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 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, 4530 mg kg^{-1} in the microalgae and 4140 mg kg^{-1} in the digestate. The digestate contained the highest levels of iron and aluminium with 30,905 mg kg^{-1} and 19,216 mg kg^{-1} respectively, that is significantly higher than the levels in found in manure and microalgae samples. The concentration of iron in swine and chicken manure was 1,040 mg kg^{-1} and 420 mg kg^{-1} respectively while the concentration of aluminium was 640 mg kg^{-1} and 762 mg kg^{-1} respectively.

3.2 Product yields during hydrothermal processing

The product yields (i.e, solid, liquid, gas and oil) following hydrothermal processing of each feedstock are shown in **Figure 1**. The product distribution is highly dependent upon process severity. The yields, residue formation, gas composition and the composition of the aqueous phase depends 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 (Lopez Barreiro et al., 2015).

In general, lower processing temperatures at 170 ℃ and 250 ℃ favour higher yields of solid residue compared to the higher processing temperatures at 350 ℃ and 500 ℃. Thermal hydrolysis at 170 ℃ typically produced the highest yields of solid residue for all the feedstock. 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. 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.%). There are very few gaseous products and no oil formation after thermal hydrolysis for all the feedstock.

Hydrothermal carbonization 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 6-12%. 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 bio-crude. 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 et al., 2012). 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; Ross et al., 2010; Biller and Ross, 2011). Various studies have shown that the HHV of the bio-crude can be enhanced using heterogeneous catalysts (Biller et al., 2011; 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 5**. 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 paper, is unaffected. The highest gaseous fraction was observed for the microalgae (55 wt.%) although the other feedstocks produce similar levels ranging from 31-33 wt.%. The levels of residue were significantly lower than lower temperature processing and ranged from 10-15 wt.% for the microalgae and manure. The digestate produced once again the highest residue due to higher levels of ash. It is well known that supercritical water gasification has a higher conversion efficiency compared to the other processing routes and it suppresses the formation of both char and tar (Xu et al., 2013).

3.3 Characterization of the solid product

Table 3 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 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. That 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 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 2**, some general trends can be identified. The level of phosphorus in the residue increase with reaction severity. This is consistently observed for each of the 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 present is 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 increases 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).

3.4 Characterization of the aqueous product (AP)

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 5**.

3.4.1 pH

The pH of the aqueous phase recovered after reaction at the different conditions is shown in **Table 5** and results in a similar trend for each feedstock. Following thermal hydrolysis, the aqueous phase was acidic, ranging between pH 4.9-5.0, 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 8.2-8.8 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; Biller et al., 2012).

3.4.2 Total Organic Carbon (TOC)

The concentrations of TOC in the aqueous phase reduces with process severity as shown in **Table 5**. 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.

3.4.3 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 2 a** and indicates that similar levels of total nitrogen (typically around 60-70 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 35% at 170 °C to 60-70% under HTL (350 °C) and SCWG (500 °C) conditions. The effect of hydrothermal processing temperature (180-240 ℃) on the nutrient behaviour in sewage sludge was investigated by Sun et al., (2013). They concluded that at lower processing temperatures (180 ℃), nitrogen solubilisation, originating from the breakdown of proteins, increased from 42% to 51% when the holding time was increased from 30-60 minutes and reaction temperature plays a dominant role in nitrogen solubilization into the aqueous phase.

Figure 4 shows the distribution of Organic N and NH_3-N in the process water 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) for SCWG of a lipid-extracted hydrochar at 450-550 ℃. At 550 °C, they achieved 90% nitrogen recovery as NH_3-N while at 600 °C 97.2% NH_3-N recovery was achieved. **Figure 3** indicates 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 ℃). The results show that 75% of the total nitrogen in the aqueous phase after thermal hydrolysis is organic. After HTC at 250 °C, it reduces to about 40-50% 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. The reason for this is not obviously apparent but will be investigated further later. A similar trend was observed in the study reported by Lopez 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.

3.4.4 Distribution of Phosphorus

Figure 2 b 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.

Further investigation of the aqueous products show that TP was made up of both organic and inorganic forms of phosphorus. **Figure 4** shows 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 ℃ and 500 ℃), 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, 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 and conclude that the 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 2)**. Some of the feedstock exhibit immobilisaion of the P whereas others behave differently. For the Swine manure and digestate, the levels of P are immobiled 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 significnt 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 2.3, 1.4 and 1.5 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 5** 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** lists the metals in the residues following 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. 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℃, P was precipitated in the solid products. This was also observed for chicken manure in the presence of Ca $(OH)_2$ (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 8.2-8.8 promoting precipitation.

3.4.5 Distribution of Potassium

The results in **Figure 2c** indicate that potassium is almost completely extracted under all conditions. Although potassium readily dissolves in water, there was an exception with chicken manure which shows only 60 wt.% recovery in the aqueous phase at 170 ℃. However as the chicken manure is extremely high in K, this may be due to saturation of the aqueous phase and the solid products retaining some of the salts. In the study by Sun et al. (2013), potassium was significantly affected with an increase in process temperature from 180-240 ℃ 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 ℃ respectively.

4.0 Conclusions

The aqueous phase following thermal hydrolysis and hydrothermal processing contains significant levels of nitrogen (N), phosphorus (P) and potassium (K). The extraction of phosphorus is feedstock dependent and linked to the presence of inorganics such as Ca, Mg and Fe. Phosphorus is typically immobilised in the residue at higher temperature processing due to precipitation of phosphate salts. Microalgae and chicken manure release phosphorus more easily than swine manure and digestate. At lower temperature processing, significant levels of organic phosphorus and nitrogen are observed in the aqueous phase. The levels of NH_3-N increase with increasing process severity.

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6.0 References

1. Berge, N.D. Ro, K.S. Mao, J. and Flora, J.R.V., 2011. Hydrothermal carbonization of municipal waste streams. Environ. Sci. Technol. 45, 5696-5703.

2. Biller, P. and Ross, A. B., 2011. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. Bioresource Technol. 102, 215-225.

3. Biller, P., Riley, R. and Ross, A. B., 2011. Catalytic hydrothermal processing of microalgae: Decomposition and upgrading of lipids. Bioresource Technol. 102, 4841-4848.

4. Biller, P., Ross, A. B., Skill, S. C., Lea-langton, A., Balasundaram, B., Hall, C., Riley, R. and Llewellyn, C. A., 2012. Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process. Algal Res. 1, 70-76.

5. Bircan, S. Y., Kamoshita, H., Kanamori, R., Ishida, Y., Matsumoto, K., Hasegawa, Y. and Kitagawa, K., 2011. Behavior of heteroatom compounds in hydrothermal gasification of biowaste for hydrogen production. Appl. Energy, 88: 4874-4878.

6. Brown, T. M., Duan, P. and Savage, P. E., 2010. Hydrothermal liquefaction and gasification of Nannochloropsis sp. Energy and Fuels, 24: 3639-3646.

7. Chen, W.-T., Zhang, Y., Zhang, J., Schideman, L., YU, G., Zhang, P. and Minarick, M., 2014. Co-liquefaction of swine manure and mixed-culture algal biomass from a wastewater treatment system to produce bio-crude oil. Appl. Energy. 128, 209-216.

8. Cherad, R., Onwudili, J.A., Ekpo, U. Williams, P.T., Lea-langton, A.R., Camargo-Valero, M. and Ross, A.B. (2013): Macroalgae supercritical water gasification combined with nutrient recycling for microalgae cultivation, Environ. Prog. and Sustainable Energy. 32, 902-909.

9. Cherad, R., Onwudili, J.A., Biller, P., Williams, P.T., Ross, A.B., (2016): Hydrogen production from the catalytic supercritical water gasification of process water generated from hydrothermal liquefaction of microalgae. Fuel 166, 24-28.

10. Dai, L., Tan, F., Wu, B., He, M., Wang, W., Tang, X., Hu, Q. and Zhang, M., 2015. Immobilization of phosphorus in cow manure during hydrothermal carbonization. J. Environ. Manag. 157, 49-53.

11. Du, Z., Hu, B., Shi, A., Ma, X., Cheng, Y., Chen, P., Liu, Y., Lin, X., Ruan, R., 2012. Cultivation of a microalga Chlorella vulgaris using recycled aqueous phase nutrients from hydrothermal carbonization process. Bioresource Technol. 126, 354–357.

12. Duan, P. and Savage, P. E., 2011. Hydrothermal Liquefaction of a Microalga with Heterogeneous Catalysts. Ind. Eng. Chem. Res. 50, 52-61.

13. Falco, C., Baccile, N. and Titirici, M.-M., 2011. Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons. Green Chem. 13, 3273-3281.

14. Funke, A. and Ziegler, F., 2010. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering, Biofuel Bioprod. Biorefine 4, 160-177.

15. He, B.J, Zhang, Y., Funk, T.L., Riskowski, G.L. and Yin, Y., 2000. Thermochemical conversion of swine manure: An alternative process for waste treatment and renewable energy production Trans. ASAE 43(6), 1827-1833.

16. He, B., Zhang, Y., Yin, Y., Funk, T.L. and Riskowski, G.L., 2001. Effects of feedstock pH, initial CO addition, and total solids content on the thermochemical conversion of swine manure. Trans. ASAE 44, 697-701.

17. Heilmann, S. M., Jader, L. R., Sadowsky, M. J., Schendel, F. J., Von Keitz, M. G. and Valentas, K. J., 2011a. Hydrothermal carbonization of distiller's grains. Biomass and Bioenergy 35, 2526-2533.

18. Heilmann, S. M., Jader, L. R., Harned, L. A., Sadowsky, M. J., Schendel, F. J., Lefebvre, P. A., Von Keitz, M. G. and Valentas, K. J., 2011b. Hydrothermal carbonization of microalgae II. Fatty acid, char, and algal nutrient products. Appl. Energy 88, 3286-3290.

19. Heilmann, S. M., Molde, J. S., Timler, J. G., Wood, B. M., Mikula, A. L., Vozhdayev, G. V., Colosky, E. C., Spokas, K. A. and Valentas, K. J., 2014. Phosphorus Reclamation through Hydrothermal Carbonization of Animal Manures. Environ. Sci. and Technol. 48, 10323-10329.

20. Jena, U., Vaidyanathan, N., Chinnasamy, S., and Das, K.C., 2011. Evaluation of Microalgae Cultivation using Recovered Aqueous Co-product from Thermochemical Liquefaction of Algal Biomass. Bioresource Technol. 102, 3380-3387.

21. López Barreiro, D., Samorì, C., Terranella, G., Hornung, U., Kruse, A. and Prins, W., 2014. Assessing microalgae biorefinery routes for the production of biofuels via hydrothermal liquefaction. Bioresource Technol. 174, 256-265.

22. Lopez Barreiro, D., Bauer, M., Hornung, U., Posten, C., Kruse, A. and Prins, W., 2015. Cultivation of microalgae with recovered nutrients after hydrothermal liquefaction. Algal Res., 9, 99-106.

23. Lu, X., Pellechia, P.J., Flora, J.R.V. and Berge, N.D., 2013. Influence of reaction time and temperature on product formation associated with the hydrothermal carbonization of cellulose, Bioresource Technol. 138, 180-190.

24. Lu, Y. and Savage, P. E., 2015. Supercritical water gasification of lipid-extracted hydrochar to recover energy and nutrients. J. of Supercrit. Fluids 99, 88-94.

25. Melero, J. A., Sánchez-Vázquez, R., Vasiliadou, I. A., Martínez Castillejo, F., Bautista, L. F., Iglesias, J., Morales, G. and Molina, R., 2015. Municipal sewage sludge to biodiesel by simultaneous extraction and conversion of lipids. Energy Convers. and Manag. 103: 111-118.

26. Mendez, L., Mahdy, A., Ballesteros, M. and González-Fernández, C., 2015. Biomethane production using fresh and thermally pretreated Chlorella vulgaris biomass: A comparison of batch and semi-continuous feeding mode. Ecol. Eng. 84, 273-277.

27. Minowa, T., Yokoyama, S.-Y., Kishimoto, M. and Okakura, T., 1995. Oil production from algal cells of Dunaliella tertiolecta by direct thermochemical liquefaction. Fuel 74, 1735-1738.

28. Mumme, J., Eckervogt, L., Pielert, J., Diakité, M., Rupp, F. and Kern, J., 2011. Hydrothermal carbonization of anaerobically digested maize silage. Bioresource Technol. 102, 9255-9260.

29. Ross, A. B., Biller, P., Kubacki, M. L., Li, H., Lea-langton, A. and Jones, J. M., 2010. Hydrothermal processing of microalgae using alkali and organic acids. Fuel 89, 2234-2243.

30. Stucki, S., Vogel, F., Ludwig, C., Haiduc, A. G. and Brandenberger, M., 2009. Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. Energy Environ. Sci. 2, 535-541.

31. Sun, X.H., Sumida, H., Yoshikawa, K., Sumida, H., Yoshikawa, K., 2013. Effects of Hydrothermal Process on the Nutrient Release of Sewage Sludge. Int. J. Waste Resources 3, 124. doi: 10.4172/2252-5211.1000124

32. Theegala, C.S. and Midgett, J.S., 2012. Hydrothermal liquefaction of separated dairy manure for production of bio-oils with simultaneous waste treatment. Bioresource Technol. 107, 456-463.

33. Titirici, M.M., Thomas, A. and Antonietti, M., 2007. Back in the black: hydrothermal carbonization of plant material as an efficient chemical process to treat the CO_2 problem? New J. Chem. 31, 787-789.

34. Toor, S. S., Rosendahl, L. and Rudolf, A., 2011. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. Energy 36, 2328-2342.

35. Tsukahara K., Kimura, T., Minowa, T., Sawayama, S., Yagishita, T., Inoue, S., Hanaoka, T. Usui, Y., and Ogi, T., 2001. Microalgal Cultivation in a Solution Recovered from the Low-Temperature Catalytic Gasification of the Microalgae. J. of Biosci. and Bioeng. 91(3), 311-313.

36. Vom Eyser, C., Palmu, K., Schmidt, T. C. and Tuerk, J., 2015. Pharmaceutical load in sewage sludge and biochar produced by hydrothermal carbonization. Science of The Total Environment 537, 180-186.

37. Xu, Z. R., Zhu, W. and Li, M., 2012. Influence of moisture content on the direct gasification of dewatered sludge via supercritical water. Int. J Hydrogen Energy, 37, 6527-6535.

38. Xu, Z., Zhu, W., Gong, M. and Zhang, H., 2013. Direct gasification of dewatered sewage sludge in supercritical water. Part 1: Effects of alkali salts. Int. J Hydrogen Energy, 38, 3963-3972.

39. Yanagida, T., Minowa, T., Nakamura, A., Matsumura, Y. and Noda, Y., 2008. Behavior of inorganic elements in poultry manure during supercritical water gasification. J. Japan Inst. Energy, 87, 731-736.

40. Yu, G., Zhang, Y., Schideman, L., Funk, T. and Wang, Z., 2011. Distributions of carbon and nitrogen in the products from hydrothermal liquefaction of low-lipid microalgae. Energy Environ. Sci. 4, 4587–4595.

41. Yu, G., Zhang, Y., Guo, B., Funk, T. and Schideman, L., 2014. Nutrient Flows and Quality of Bio-crude Oil Produced via Catalytic Hydrothermal Liquefaction of Low-Lipid Microalgae. BioEnergy Res. 7, 1317-1328.

42. Zhu, W., Xu, Z.R., Li, L. and He, C., 2011. The behavior of phosphorus in sub- and super-critical water gasification of sewage sludge. Chem. Eng. J. 171, 190-196.

Table 1: Proximate and ultimate analyses of the various biomass samples

Biomass	**Proximate analyses (%)**				**Ultimate analyses [a] (%)**					
	Moisture	Ash [a]	Volatiles	Fixed carbon [a]	C	H	N	S	O[b]	HHV (MJ Kg^{-1})
C. vulgaris	5.1	11.5	78.5	11.3	47.7	7.0	9.9	0.5	23.5	22.0
Digestate	3.2	63.0	32.2	2.2	18.4	2.9	2.7	0.3	12.7	8.2
Swine manure	7.2	10.0	83.5	n/d	47.3	6.5	3.1	0.2	32.9	19.5
Chicken manure	5.4	10.5	73.8	10.9	43.8	6.4	5.7	0.2	33.4	18.1

[a] dry basis

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

n/d not determined

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

Biomass	**Concentration (mg/Kg)**							
	P [c]	**K** [b]	**Ca** [b]	**Mg** [b]	**Na** [b]	**Ni** [a]	**Fe** [b]	**Al** [b]
C. vulgaris	22580	4530	16810	5310	7650	450	2810	2570
Digestate	16430	4140	23580	5100	6410	420	30910	19220
Swine manure	15580	8060	36770	9600	3950	510	1040	640
Chicken manure	12870	20300	24300	6510	3670	200	420	760

[a] analysis by ICP-MS
[b] analysis by AAS
[c] analysis by colorimetry

Table 3: Proximate, Ultimate analysis and HHV of residues

Conditions	Proximate analyses (%)				Ultimate analyses [a] (%)					
	Moisture	Ash [a]	Volatiles	Fixed carbon [a]	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
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

[a] dry basis

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

[nd] not detected

Table 4: Nutrient and metal in the recovered residues (dry basis)

	Concentration (mg/Kg)							
Conditions	P[c]	K[b]	Ca[b]	Mg [b]	Na [b]	Ni [a]	Fe [b]	Al [b]
C.vulgaris								
Hyd 170°C	21240	250	26060	7650	3650	140	6190	4850
HTC 250°C	93100	1740	98280	33860	5360	240	14090	16540
HTL 350°C	157200	15610	146250	48140	10900	240	27010	23880
SCWG 500°C	118500	12300	107360	39420	35060	6250	18010	22380
Digestate								
Hyd 170°C	17210	2650	24660	6400	4520	230	35260	20270
HTC 250°C	19330	3030	28140	7050	3930	240	38770	22890
HTL 350°C	19340	3490	29340	7710	4390	240	40280	23770
SCWG 500°C	20200	5310	30100	7900	6280	1540	41650	24000
Swine manure								
Hyd 170°C	15490	220	39950	5890	5050	110	1580	1350
HTC 250°C	29610	190	55900	9820	5150	120	2220	1660
HTL 350°C	39470	230	81070	20540	5230	200	3690	2300
SCWG 500°C	52710	1140	114090	32840	17700	7630	4090	4520
Chicken manure								
Hyd 170°C	14030	200	35410	4510	4980	120	1270	1650
HTC 250°C	24490	350	47780	11260	5620	110	1510	1970
HTL 350°C	40230	740	61740	19040	6758	130	2120	2090
SCWG 500°C	63690	9740	85870	32700	33690	31060	1920	6590

a analysis by ICP-MS
b analysis by AAS
c analysis by colorimetry

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

		Concentration (mg/Kg)			
Conditions	pH	TOC	Total N	Total P	Total K
C.vulgaris					
Hyd 170°C	5.0	196870	47960	8510	4850
HTC 250°C	7.1	179120	60390	8370	3820
HTL 350°C	8.3	94640	62040	6450	2850
SCWG 500°C	8.8	83370	55690	3070	5240
Digestate					
Hyd 170°C	5.1	65740	19560	1360	2330
HTC 250°C	7.7	62350	18610	840	2340
HTL 350°C	8.2	46980	17110	560	2040
SCWG 500°C	8.7	34170	13780	600	1440
Swine manure					
Hyd 170°C	4.9	118180	10640	2060	8120
HTC 250°C	5.9	101840	12790	650	7890
HTL 350°C	6.7	80780	15820	800	7790
SCWG 500°C	8.2	44510	19970	710	6050
Chicken manure					
Hyd 170°C	5.0	184180	33430	5250	19030
HTC 250°C	7.2	141120	32770	1470	19080
HTL 350°C	8.0	102800	31700	820	18520
SCWG 500°C	8.5	48670	34300	1060	12600

Typical pH values ± 0.1

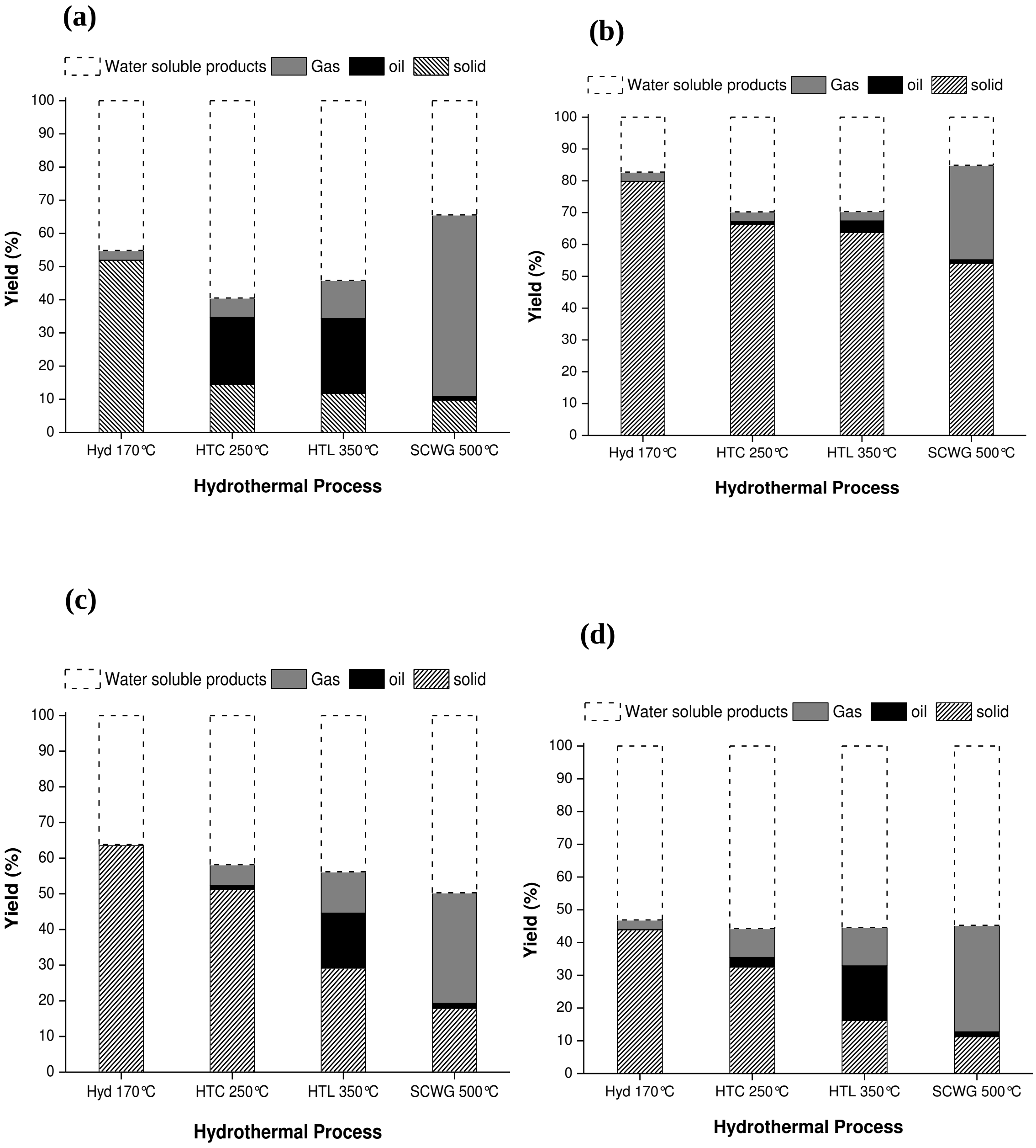

Figure 1: Product distribution during hydrothermal processing of a) C.vulgaris b) digestate c) swine manure d) chicken manure

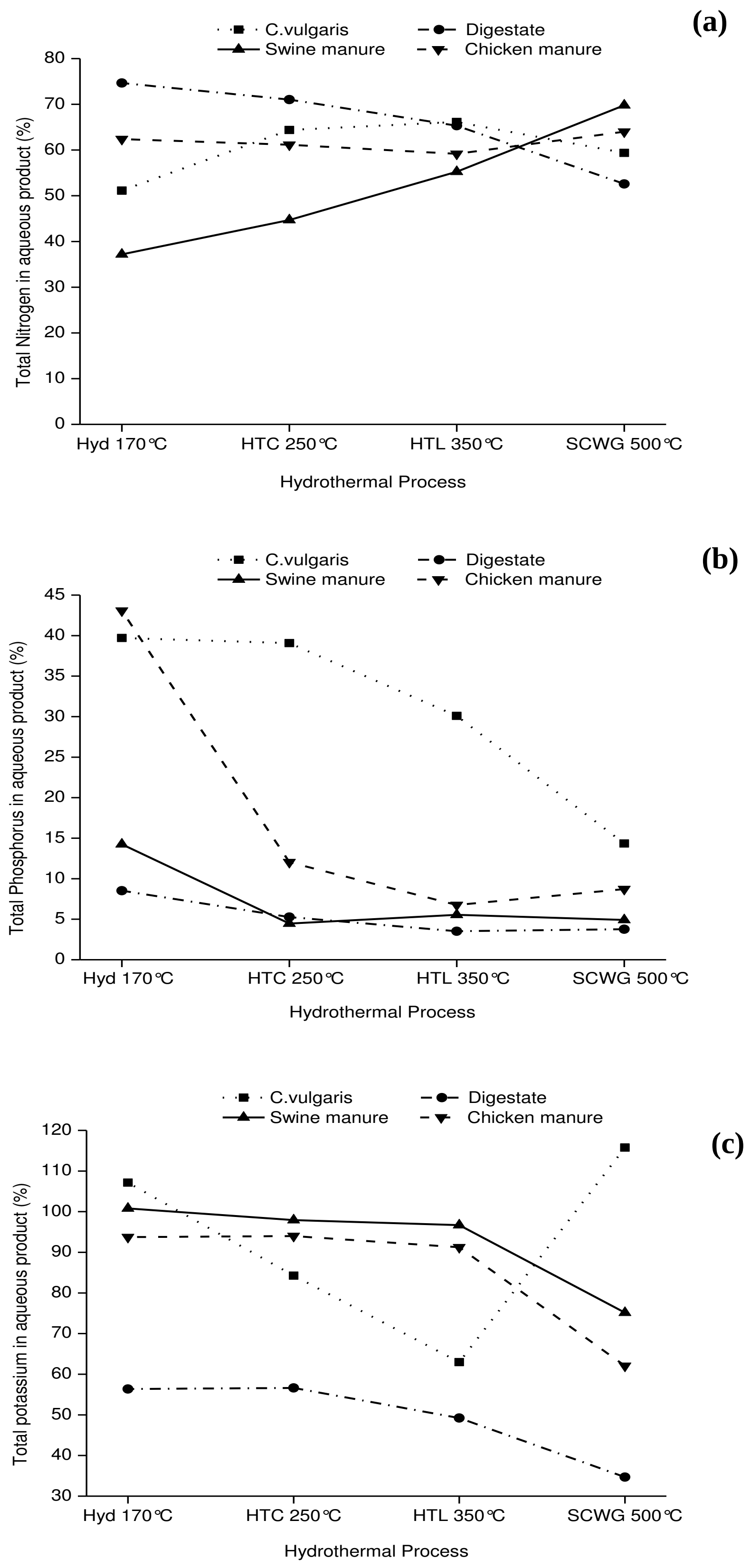

Figure 2: Extraction of nutrients into the aqueous phase (a) extraction of Total N (b) extraction of Total P (c) extraction of Total K

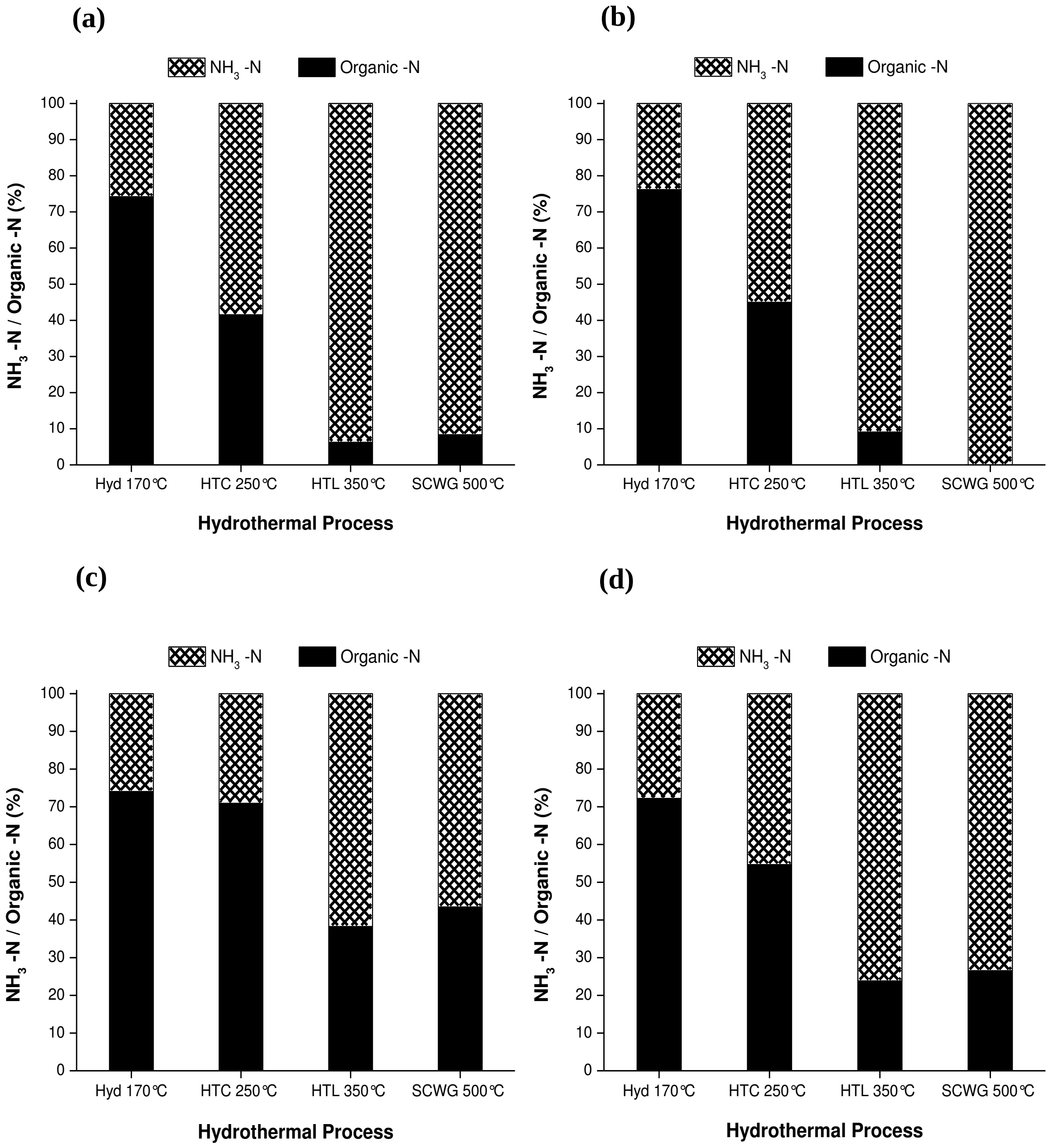

Figure 3: Forms of nitrogen present in the aqueous products from a) C.vulgaris b) digestate c) swine manure d) chicken manure

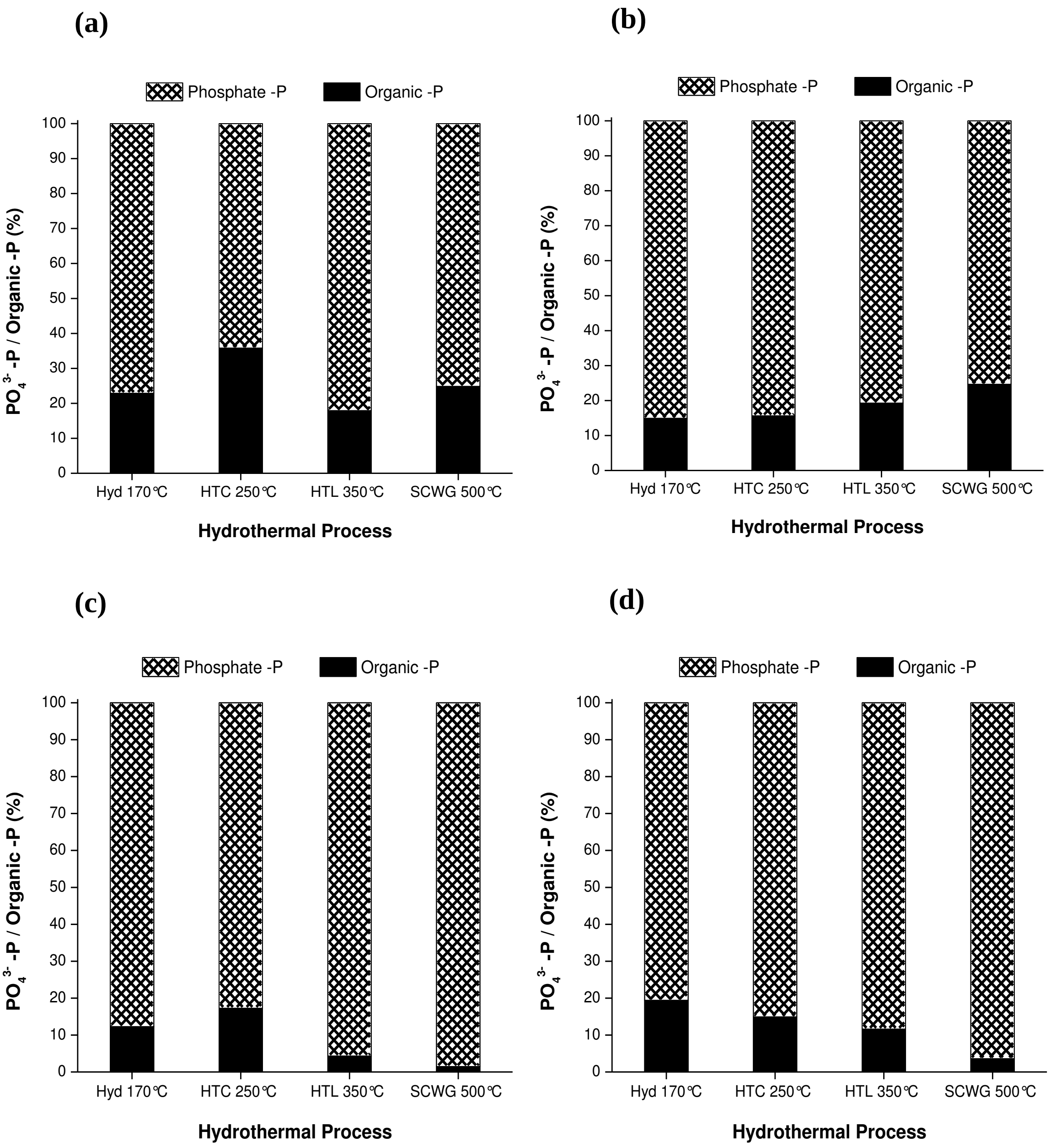

Figure 4: Forms of phosphorus present in the aqueous products from a) C.vulgaris b) digestate c) swine manure d) chicken manure