

Chicken Manure for Biofuels and Biobased Chemicals



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This BSc thesis has been carried out during the COVID-19 global pandemic (spring-summer 2020). In order to comply with all the learning goals specified for the BSc final project in Chemical Engineering at the University of Groningen, (some of) the results presented in this thesis were not experimentally obtained but provided by the main supervisor based on previous unpublished data and personal experience, or obtained from published literature. The source of data has also been specified explicitly or referenced wherever they appear in this text.

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Abstract

This study aimed to investigate the potential of a novel biorefinery involving chicken manure, an abundant agricultural waste product. The role of this biorefinery is to produce biofuels using hydrothermal liquefaction (HTL) as well as recover uric acid (UA) and phosphates as valuable chemicals. The viability of the biorefinery was analysed by means of an extensive literature overview.

Chicken manure proved to be a promising feedstock for HTL to produce an energy-rich biocrude product, with lab-scale studies having achieved yields of up to 17.7 wt% (dry basis). The tests analysed were performed in batch reactors (75-300 ml), at subcritical water conditions (310-350°C, 18-20.5 MPa) and retention times of 15-60 minutes. The higher heating values (HHV) of biocrudes ranged from 32.0-37.0 MJ/kg, which are significantly higher than the original feedstocks (10.7-18.1 MJ/kg). Furthermore, available upgrading techniques proved that upgrading to modern-day fuels, especially biodiesel, was achievable while being economically competitive to other biofuel technologies. Next, uric acid extraction prior to HTL is possible using several integration methods, with UA yields above 80% and purities of up to 99.9% attainable. Moreover, a large fraction of the solid residues involved in the process have feed and supplement value which suggests they are suitable for HTL processing. Finally, the phosphate analysis established that insoluble calcium phosphates are the predominant phosphorus species formed during HTL of chicken manure. These species have been proven to be readily extractable, with recoveries of greater than 90% achieved from the hydrochar product, and are notably the desired constituents of diminishing phosphate rock reserves.

It was concluded that such a biorefinery has great potential in producing functional modern-day fuels and recovering valuable chemicals from chicken manure while alleviating contamination-related disposal concerns. Furthermore, the HTL studies investigated were not performed at experimentally determined optimal conditions or on a continuous basis, which implies that considerable optimisations can still be made. Considering the potential economic benefits of combined uric acid and phosphate extraction with HTL, along with new developments in HTL operations as well as possible government support; such a biorefinery could prove feasible in the near future.

This investigation provides a review on HTL processing of chicken manure and may be used as the basis for further work on HTL technology. The result of this work is expected to contribute to the development of efficient biorefining concepts involving chicken manure. These findings may further be used to valorise common waste streams for energy generation and chemical recovery, which could have positive impacts on local development.

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Introduction

Exponential growth of the human population has led to an increased demand for high protein sources such as meat and eggs, which has consequently resulted in the massive expansion of global chicken industries as seen in Figure 1 below [1]. Currently, the poultry sector is one of the fastest growing agricultural domains, with chickens being the most widespread domestic animal and as such producing massive amounts of waste [2]. In 2008, Brazil alone generated 11 billion kilograms of chicken manure [3].

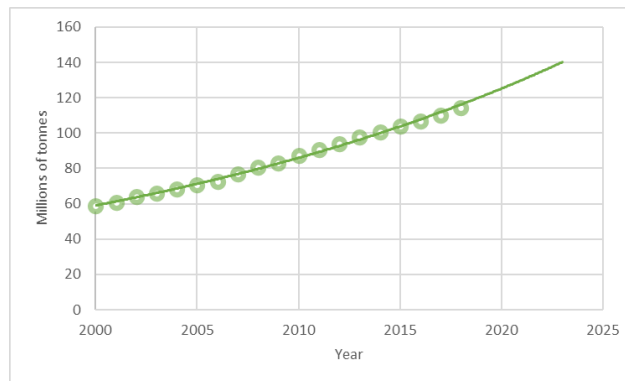


Figure 1: Showing the exponential growth of chicken meat production globally. Adapted from [79].

Chicken Manure Disposal

Chicken manure is primarily disposed of by land application as a fertilizer and has minor applications in the production of biogas as well as energy via incineration [2,5]. It is predominantly applied on land due to its organic and nutrient value and because it is an inexpensive disposal method [2,5,10]. However, modern farming practices, such as concentrated animal feeding operations (CAFOs) as seen in Figure 2 below, have made land application of chicken manure increasingly unsustainable with growing environmental concerns [3,5,6].



Figure 2: Showing the over-crowded nature of modern-day concentrated farming operations [98]

Chicken manure is an excellent soil amendment that provides essential plant nutrients such as nitrogen, phosphorus, calcium and organics [4]. However, it also contains significant amounts of heavy metals, pathogens, growth hormones, harmful trace elements, pesticides as well as antibiotic resistance genes that can have deleterious effects on the environment and human health when discharged without appropriate treatment [2,3,7]. Many of these constituents originate from chicken feed and from chemicals used to treat diseases in commercial facilities [7]. Rainfall carries excess nutrients from the land, contaminating both ground and surface waters, resulting in effects such as eutrophication of water bodies and the consequent death of ecosystems [9]. Additionally, the accumulation of heavy metals in the soil

results in the uptake of these heavy metals by crops which consequently adversely affects the consumers of these products [2,5,8]. Furthermore, the storage and application of chicken manure results in green-house gas (GHG) emissions, nitrate pollution, public nuisances as well as the production of phytotoxic substances [6,7,9].

Based on these disposal issues, the development of new manure management systems would prove highly beneficial. Furthermore, chicken manure is a potential source of renewable energy and valuable chemical constituents. This suggests that it can be treated to prevent environmental damage and reduced human health concerns, while also providing a source of clean energy and useful chemicals.

Hydrothermal Liquefaction (HTL)

Hydrothermal liquefaction is an emerging thermochemical technique used to valorise wet biomass, ranging from algae to lignocellulostics and other organic wastes. HTL was developed in the 1970s following the oil crisis, which promoted the emergence of alternative energy-provision methods [11]. HTL involves the reaction of organic material in the presence of water, which acts as a solvent and catalyst, at moderate temperatures (250-450°C) and high pressures (10-35 MPa) for 0.2-1.5 hours [11]. However, HTL is usually performed at subcritical conditions (<374°C) due to energy-cost inhibitions associated with supercritical operation [11]. HTL results in the production of an energy-rich oil (biocrude) as well as solid (hydrochar), aqueous and gaseous by-products.

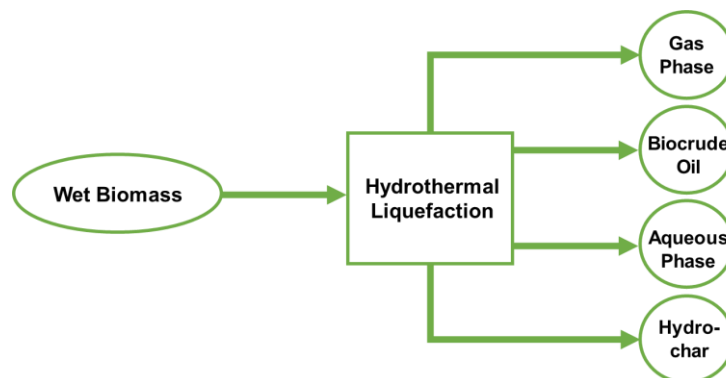


Figure 3: Schematic representation of the HTL process

HTL has several benefits over other thermochemical conversion techniques. It does not require the energy-intensive step of drying the feedstock which gives larger feedstock flexibility, the biocrude oil produced has a relatively low oxygen content making it more suitable as a biofuel and also the heat of vaporisation is avoided during the process as water is kept in the liquid state due to the high pressures [9]. Furthermore, HTL has proven advantageous as it kills pathogens present in the feed, uses an environmentally friendly solvent, produces a carbon neutral biofuel and removes odorous compounds among other benefits [9,11,12]

HTL has great potential for manure management and has seen increasing attention in recent years for such purposes [13]. In addition to providing a clean energy source, HTL has also proven to be a promising method for aiding the extractability of valuable compounds in the feedstock [12].

Uric Acid

Uric acid is a major constituent of chicken excreta and thus chicken manure. It is a heterocyclic compound consisting of carbon, oxygen, nitrogen and hydrogen with the chemical formula $C_5H_4N_4O_3$. Uric acid is a purine-derivative formed during the metabolic degradation of purine

nucleotides (adenine and guanine) and is primarily synthesised in the liver, intestines and vascular endothelium [15].

Uric acid is commercially obtained from sources such as marine guano, reptilian faeces and other bird faeces and is extensively utilised in research laboratories to study various animal and human diseases [72]. Uric acid is known for its inflammatory actions as well as antioxidative and neuroprotective properties and is involved in several clinical trials [16,18]. Furthermore, uric acid is an attractive component of chicken manure as it commonly plays a role in the synthesis of high-value purines as well as other chemicals that have key applications in the food, cosmetic and pharmaceutical industries [19,20]. These chemicals include caffeine, allantoin, xanthine, theobromine, alloxan, murexide and parabanic acid among others [19,20]. Uric acid is a high-valued commodity, selling for approximately \$12000 per tonne. This makes its recovery highly attractive, especially when considering expanding food, cosmetic and pharmaceutical industries [21].

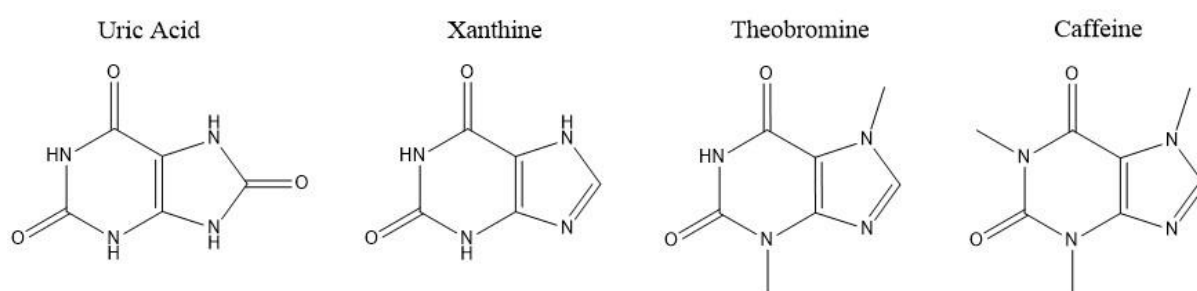


Figure 4: Showing the structural similarities between uric acid, xanthine, theobromine and caffeine

Phosphates

Phosphorus is an element essential for life, as it plays a key role in the metabolism of all living cells [9]. It is predominantly obtained from non-renewable sources of phosphate rock, which are mined from highly concentrated deposits with approximately 80% of the world's reserves located in Morocco, South Africa, China and the USA alone [9, 22].

Phosphate rock contains calcium phosphate species such as apatites ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$) and tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), of which a majority is used in the fertilizer industry where they are the primary source of phosphorous [23]. These calcium phosphate species as well as their derivatives also play a key role in food and beverages, cosmetics, medical products, pharmaceuticals and will be crucial in the emerging biofuels market [9]. Calcium phosphate species are compounds consisting fundamentally of phosphorous, calcium and oxygen and for the most part are interconvertible through different treatments [23].

Phosphate rock reserves have received major concerns as estimates suggest they could be depleted in the next 50-100 years, with peak phosphorus supply occurring as soon as 2030 [24, 25]. Additionally, a great amount of phosphorous is lost in the food chain through manure, human excreta and other organic wastes causing the phosphorous cycle to become increasingly linear [22]. A large majority ends up in water bodies where it cannot be retrieved, causing widespread pollution and contributing to dead zones in seas and rivers through eutrophication [22].

Due to this, major efforts are being made to implement efficient reclamation processes especially in areas such as the EU where they have declared phosphate rock and phosphorus as critical raw materials, which suggests that they are essential resources with a risk to supply [26]. Given the concentrated nature of phosphate reserves, many areas including the EU

obtain almost all their phosphorus through imports [22, 26]. Due to this uneven distribution, phosphorus depletion could also lead to major geopolitical tensions in the future [24].

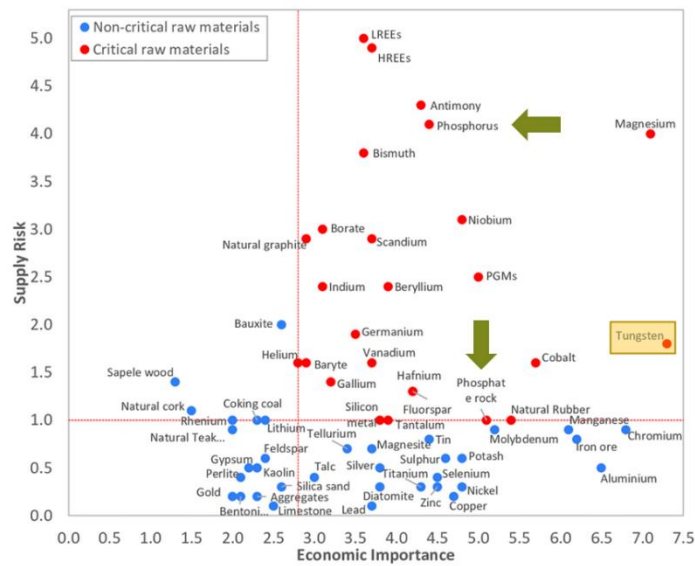


Figure 5: Showing the classification of EU raw materials with phosphorus and phosphate rock declared as “Critical raw materials”. Adapted from [26].

Overall, the shortage of phosphates will adversely affect food availability, prices and thus global food security. Efficient phosphorus recovery techniques are vital in order to reduce pressure on limited reserves, sustain food security while additionally alleviating contamination-related problems. Furthermore, considering the fourfold increase in phosphate demand over the last century, the recovery of phosphates is a highly attractive opportunity in terms of profitability too [24].

Biorefinery

A biorefinery is a facility that integrates the biomass conversion process to produce biofuels as well as obtain biobased chemicals and is analogous to a petroleum refinery [14]. This study aimed to investigate a novel biorefinery scheme involving chicken manure and can be seen in Figure 6 below. The role of this biorefinery is to produce biofuels using hydrothermal liquefaction as well as recover uric acid and phosphates. The following sections discuss the composition of chicken manure, the current state and knowledge of HTL operations, HTL processing of chicken manure as well as the compatibility of combined uric acid and phosphate extraction with HTL. Major focus is placed on the biofuel analysis (1) and the recovery of uric acid (2) and phosphates (3) as biobased chemicals. The prospects of this biorefinery were assessed using relevant publications in order to determine the implications and possibilities involved in implementing the facility.

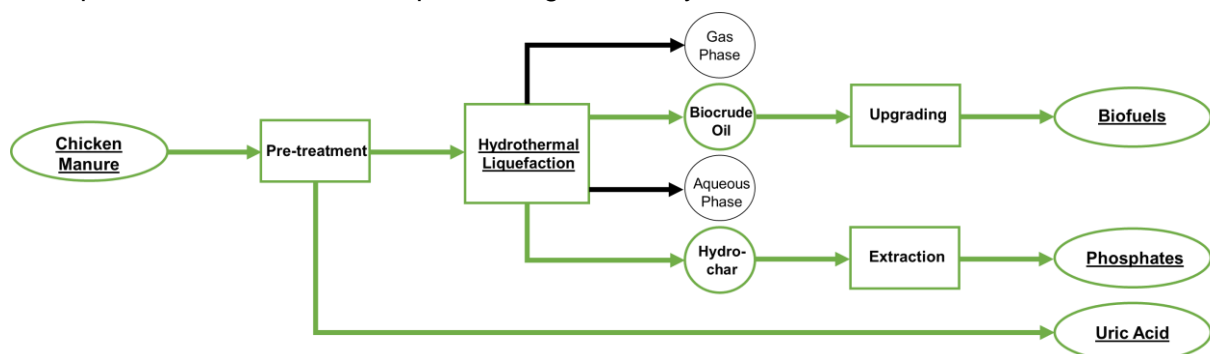


Figure 6: Schematic representation of the biorefinery under investigation

Results/Literature Overview and Discussion

Chicken manure composition

Chicken manure is the term used to represent the manures produced by layers (raised for eggs) and broilers (raised for meat). Out of all livestock manures, it is one of the richest in terms of nitrogen, phosphorus and potassium content [29].

The composition of chicken manure varies but generally consists of chicken excreta, bedding, spilled feed, water, feathers and soil [3,9,10]. Furthermore, it contains organic contents such as proteins, lipids, lignin and carbohydrates (cellulose and hemicellulose) as well as heavy metals, pathogens and trace elements among others [7,25]. Chicken manure, as with other manures, does not contain a dominant class of compounds [32]. Moreover, the composition of the manure is affected by several factors including diet, nature and quantity of bedding, age of chickens, type of chicken, climate, time between excretion and collection as well as the storage method used [10, 31].

Currently, there are very few publications available dealing with the processing of chicken manure via hydrothermal liquefaction [30]. As a result, this investigation additionally focuses on the processing of poultry manures in order to reach more informed conclusions. Poultry was deemed suitable in this investigation as it refers to domesticated fowls, including chickens which are the most widespread poultry species [79].

Due to the varying nature of manure compositions, an indication of typical values has been given in Table 1 below. These values were obtained from several sources and are based primarily on the HTL samples used in literature.

Table 1: Showing the properties of manures pertinent to this study

	Chicken manure	Poultry Manure	Broiler Manure	Laying Hen Manure
Proximate Analysis (wt%)				
Moisture	5.40 – 8.20	22.8 – 26.0	73.4	75.9
Ash^A	10.5 – 15.4	15.3	22.0 – 34.7	28.0 – 38.0
Volatiles^A	60.2 – 73.8	61.0	-	-
Fixed Carbon^A	10.9 – 21.5	15.0	-	-
Biochemical Analysis (wt%)^A				
Lipid	2.37	2.10	4.41 – 6.75	3.77 – 6.46
Protein	18.6 – 33.1	31.6 – 48.4	17.0 – 25.7	11.6 – 23.6
Hemicellulose	19.9	18.3 – 21.5	16.0 – 33.7	17.0 – 34.8
Cellulose	11.39	7.70 – 12.0	11.0 – 30.8	15.0 – 32.8
Lignin	5.23	2.30 – 7.20	1.35 – 4.00	1.51 – 3.00
HHV (MJ/kg)	16.0 - 18.1	11.7	10.7	11.7
Elemental analysis (wt%)^A				
C	40.2 – 43.9	34.1 – 41.3	29.9	32.8
H	5.40 – 6.50	4.42 – 5.50	3.80	4.12
O	32.8 – 33.4	28.0 – 42.7	28.9	22.4
N	2.81 – 5.70	2.89 – 4.40	2.67	2.52
Ca (g/kg)	24.3	23.6 – 40.6	-	-
P (g/kg)	12.9	18.1 – 19.1	-	-
K (g/kg)	20.3	-	-	-
Mg (g/kg)	3.00 – 4.90	4.00 – 4.20	-	-
Sources Used	[9], [32], [38], [81]	[33-37], [42]	[13], [31], [39]	[13], [31], [39]

Note: ^A Dry basis (db), only the predominant inorganic elements are mentioned.

As can be seen in Table 1, all manures show high levels of proteins (>11.6% db), hemicellulose (>16.0% db) and cellulose (>7.70% db) with relatively low levels of lipids (<6.75% db) and lignin (<7.20% db). They also show high levels of volatiles (>61% db) as well as carbon (>29.92% db) and oxygen (>22.43% db) content.

Hydrothermal Liquefaction

Hydrothermal liquefaction involves the conversion of wet biomass under elevated temperatures (250-450°C) and high pressures (10-35 MPa). As mentioned previously, this treatment results in the formation of biocrude oil as well as solid (hydrochar), aqueous and gaseous by-products.

Under hydrothermal conditions, the properties of water change which facilitates the desired liquefaction reactions. The dielectric constant of water drops by approximately 80% in the subcritical region, thereby allowing the dissolution of non-polar compounds where it acts as an organic solvent [11]. Additionally, subcritical water is capable of catalysing both acidic and basic reactions by dissociating into hydrogen and hydroxyl ions, respectively. This can be seen by the increase in equilibrium constant/ionic product (K_w) to around 10^{-11} at 200-300°C compared to 10^{-14} at room temperature [9]. Furthermore, despite the drop in ionic product for water in the supercritical region, the influence of pressure allows for conditions favouring liquefaction rather than gasification even at supercritical conditions [11]. This can be seen in Table 2 below, where an increase from 25 to 50 MPa in the supercritical region results in a decrease in pK_w , and as such an increase in K_w , to levels resembling subcritical water.

Table 2: Showing the properties of water at standard, subcritical and supercritical conditions with varying pressures. Table is adapted from [87].

	Typical Water	Subcritical Water		Supercritical Water	
Temperature (°C)	25	250	350	400	400
Pressure (MPa)	0.1	5	25	25	50
Density (g/cm³)	1	0.8	0.6	0.17	0.58
Dielectric constant (F/m)	78.5	27.1	14.1	5.90	10.5
Ionic product (pK_w)	14	11.2	12	19.4	11.9
Dynamic viscosity (mPa.s)	0.89	0.11	0.064	0.03	0.07

Currently, HTL has been predominantly performed using a batch system as it is still primarily operated on a lab-scale for research purposes [30]. This set-up commonly involves stirred tank reactors with volumes ranging from a few hundred millilitres to several litres [30]. The approach usually involves the initial drying and grinding of feedstock, followed by the addition of water to reach a desired solid weight fraction. Thereafter the wet biomass is fed into the reactor with the desired operating environment (catalysts, process gases and solvents among others). The reactor is then heated to the desired temperature and pressurised for the chosen retention time before being cooled down [11]. The products are consequently collected and analysed [11].

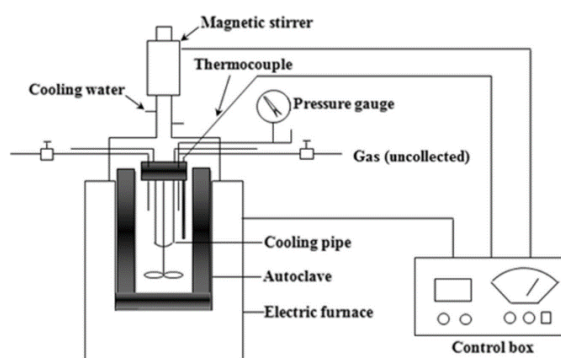


Figure 7: Showing a common lab-scale setup of HTL [88]

Reactions Involved in Hydrothermal Liquefaction

The reaction mechanisms involved in HTL remain largely unclear due to the complexity of feedstocks and HTL products as well as the numerous possible intermediate reactions [40]. However, currently it is generally accepted that the organic content initially undergoes fragmentation by hydrolysis, followed by further degradation through several reactions including depolymerisation, hydrogenolysis, dehydration, dehydrogenation, deamination and decarboxylation [11,40-42]. Thereafter repolymerisation and recombination reactions occur between reactive fragments, including various condensation mechanisms, to form products part of the biocrude and hydrochar [11,40-42]. The superheated properties of water facilitate these reactions where it acts as an organic solvent and catalyst with reduced mass transfer resistance [43]. Additionally, the high pressure facilitates degradation as it aids the penetration of water molecules into the biomass structures [43].

The decomposition of macromolecules such as cellulose, hemicellulose, lignin, proteins and lipids have been extensively studied and are summarised as follows. Amongst lignin, cellulose and hemicellulose; lignin is the most stable due to its high degree of polymerisation and complex branching, making its chain difficult to fracture [44, 45, 46]. Lignin results in the predominant formation of hydrochar when undergoing HTL, whereas hemicellulose and cellulose produce a greater biocrude yield [45]. The structures of cellulose and hemicellulose show relatively weak hydrogen bonding which gives them lower thermal stability and consequently higher degradability in HTL [44]. For cellulose and hemicellulose, hydrolysis occurs at hydrothermal conditions resulting in oligomers and monomers which are then consequently reacted further to other derivatives [41]. Lastly, hemicellulose is more easily degraded in comparison to cellulose due to its more amorphous structure [45].

Under hydrothermal conditions, lipids are easily hydrolysed to form several products including fatty acids [41]. These acids are then further degraded to form species such as amides, alkanes and alkenes which are found in conventional fuels, which makes lipids highly attractive for HTL [41]. Furthermore, proteins also undergo rapid hydrolysis at hydrothermal conditions [40]. The peptide bonds (C-N) responsible for protein formation are hydrolysed to amino acids (monomers) [40]. These monomers are then further reacted through various pathways such as decarboxylation and deamination to form a variety of products including ammonia and carbon dioxide [40, 41].

Overall, it has been confirmed that biocrude yields are greatest when the manure has a composition in the order lipids > proteins > hemicellulose > cellulose > lignin [13]. The high levels of volatiles, proteins and hemicellulose as well as the low levels of lignin make chicken manure an attractive feedstock for HTL to yield significant biocrude.

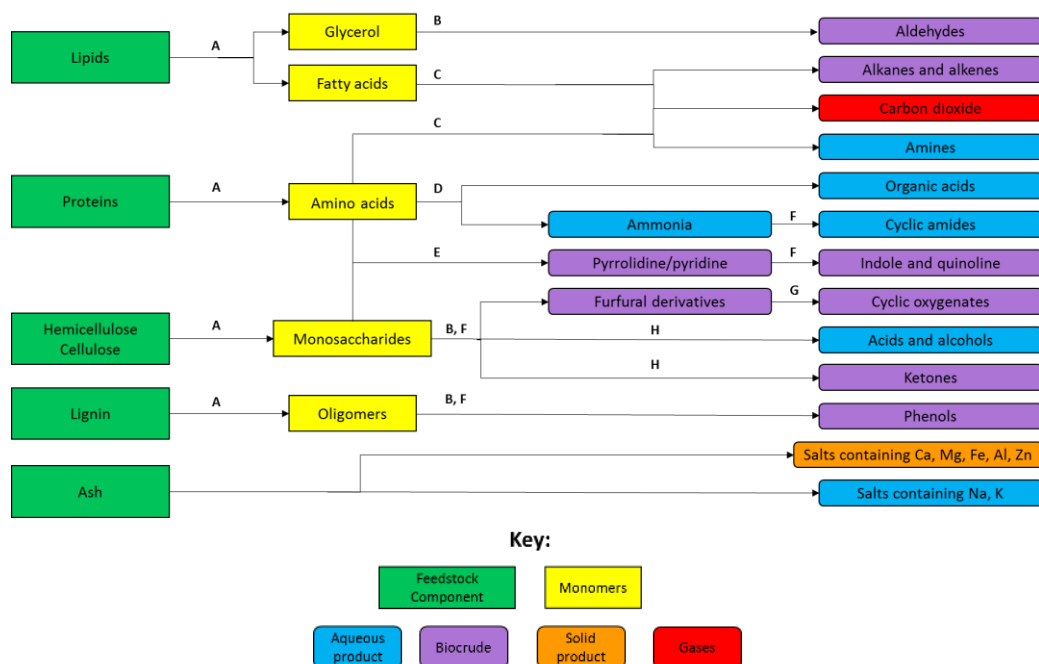


Figure 8: Overview of a few potential reaction pathways for chicken manure constituents under HTL conditions. (A: hydrolysis, B: dehydration, C: decarboxylation, D: deamination, E: Maillard reaction, F: cyclization, G: polymerisation, H: decomposition). Adapted from [50].

Hydrothermal Liquefaction Operating Conditions

The conditions at which HTL is operated significantly influence the distribution of products as well as their compositions. These conditions are strongly dependent on the feedstock type and have varying levels of influence. The major parameters influencing HTL include temperature, feedstock composition and properties of the additional solvent used [45, 46]. The moderately influencing parameters include residence times, initial as well as final pressure, catalysts used and the reaction atmosphere (reducing gases/hydrogen donors), while low influencing parameters include biomass particle size as well as heating rate [45].

Altering these parameters is essential in order to find the optimum HTL processing conditions for the feedstock in question. This allows for maximising biocrude yield and quality as well as minimising hydrochar and gas formation. Temperature is one of the most influential factors in HTL because sufficient energy is required for decomposition of organic matter to occur, while excessive energy promotes the condensation and decomposition of biocrude formed into hydrochar and gaseous products respectively [44, 47]. Furthermore, temperature also affects the carbon and oxygen content of the biocrude which consequently affects its higher heating value (HHV) and thus suitability as a biofuel [44, 46]. Based on studies performed using swine and dairy manures, it was found that the most effective temperature was in the range of 300-350°C, depending on the other conditions, in order for degradation to occur sufficiently [42, 47].

Overall, longer residence times, higher initial pressures and mass ratios larger than 35 wt% (solids) have been proven to decrease biocrude yield due to favoured gaseous and hydrochar formation [9,30, 47]. It has also been suggested that a 4-10 mm particle size is optimum to allow greater accessibility for fragmentation, while at a reasonable grinding cost [45]. Hydrogen-donor and organic solvents (such as tetralin, methanol and ethanol) as well as reducing gases (such as carbon monoxide and hydrogen) have been proven to increase biocrude yields. They do so by stabilising the biocrude formed and as such prevent polymerisation reactions that form hydrochar and decomposition reactions that form gases

[43, 46, 48]. Hydrogen-donor solvents have proven more effective because reducing gases often rely on the presence of certain catalysts to function efficiently [45]. Furthermore, the use of alkaline catalysts (such as sodium carbonate and potassium hydroxide) have been proven to increase biocrude yield and quality, reduce reaction temperature and pressure as well as decrease hydrochar formation [9, 44]. Lastly, a moderate heating rate is usually beneficial for biocrude yields, as excessively high rates favour gaseous formation and low rates favour hydrochar formation [44].

Current State of HTL and Continuous Operations

HTL has been proven to be an attractive pathway for wet biomass valorisation, but it remains largely in the experimental phase [44, 46]. Currently, only a few HTL operations have gone beyond lab and bench scale, which is critical for industrialization [54]. Overall, HTL is in the transition between lab/pilot scale and industrial implementation, with some studies suggesting it is rapidly approaching commercial status [51]. Recently there have been more studies concerning continuous HTL operation, with several companies active in its commercialisation by having built demonstration units [11]. However, there is limited data available on these operations in open literature, for confidentially reasons, and none have reached commercial scale or status [11].

Continuous operation of HTL has proven beneficial in improving efficiency and yields of biocrude through methods such as recycling unreacted feedstock and the use of heat integration mechanisms [11, 51]. Examples of some near-commercial, continuously operated HTL facilities include Hydrofaction™ which was developed by the Danish-Canadian company Steeper Energy in collaboration with Aalborg University, Cat-HTR™ which was developed by an Australian company Licella Pty Ltd and Green2Black™ which was developed by Australian company Muradel Pty Ltd [11]. These operations predominantly deal with agricultural and industrial residues. However, an upcoming pilot plant is currently under construction by Aarhus University in which continuous HTL operation will be performed using manures and sewage sludge to produce biocrude as well as obtain phosphorus [89]. This is pertinent to the biorefinery in question and as such shows promise for future viability and implementation.

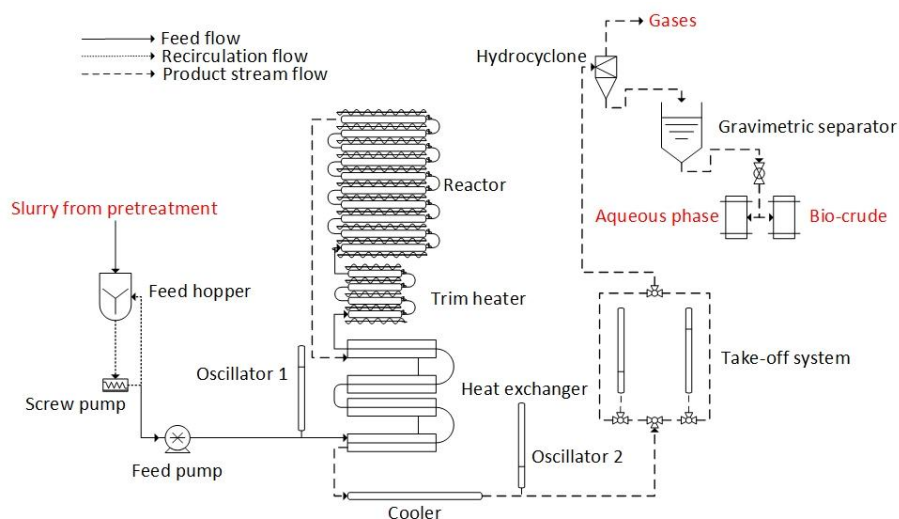


Figure 9: Simplified diagram of the continuous HTL pilot plant at Aarhus University [90]

Chicken Manure as a Feedstock for HTL

Table 3: Showing the HTL conditions and major results from all studies found dealing with chicken or poultry manures

	[37] and [42]	[9] and [32]	[13]	[13]	[2]	[2]	[39]	[39]
Feedstock	Poultry Manure	Chicken Manure	Laying Hen Manure	Broiler Manure	Laying Hen Manure	Broiler Manure	Laying Hen Manure	Broiler Manure
Reactor	300 mL Batch	75 ml Batch	100 mL Batch	100 mL Batch	100 mL Batch	100 mL Batch	100 mL Batch	100 mL Batch
Temperature (°C)	350	350	310 and 340	310 and 340	310	310	310 and 340	310 and 340
Pressure (MPa)	20.5	18	NS	NS	NS	NS	NS	NS
Catalyst	1 g Na ₂ CO ₃	-	-	-	-	-	-	-
Retention time (min)	15	60	30	30	30	30	30	30
Process gas	CO	-	-	-	-	-	-	-
Solids (wt %)	20	10	20	20	NS	NS	20	20
Agitation (RPM)	200	NS	NS	NS	NS	NS	300	300
Heating rate (°C/min)	10	10	6-8	6-8	NS	NS	NS	NS
Aqueous yield (wt%)^A	-	55.5	40.5 (310°C) 43.7 (340°C)	45.2 (310°C) 48.7 (340°C)	-	-	40.7 (310°C) 42.7 (340°C)	45.2 (310°C) 48.8 (340°C)
Gaseous yield (wt%)^A	-	11.5	8.70 (310°C) 6.90 (340°C)	7.90 (310°C) 8.20 (340°C)	-	-	8.50 (310°C) 7.10 (340°C)	7.90 (310°C) 8.00 (340°C)
Hydrochar yield (wt%)^A	21.0	16.0	37.1 (310°C) 36.6 (340°C)	35.9 (310°C) 33.9 (340°C)	-	-	37.1 (310°C) 36.8 (340°C)	35.9 (310°C) 33.8 (340°C)
Biocrude yield (wt%)^A	17.7	17.0	13.7 (310°C) 12.8 (340°C) 20.8 (310°C) ^B 15.5 (340°C) ^B	11.0 (310°C) 9.20 (340°C) 19.0 (310°C) ^B 15.5 (340°C) ^B	21.01 ^B	17.77 ^B	13.7 (310°C) 13.4 (340°C)	11.0 (310°C) 9.40 (340°C)
Biocrude HHV (MJ/kg)	32.0	-	36.2 (310°C) 37.0 (340°C)	36.5 (310°C) 36.8 (340°C)	-	-	-	-
Hydrochar HHV (MJ/kg)^A	-	25.4	-	-	-	-	-	-
Feedstock HHV (MJ/kg)^A	11.7	18.3	-	-	-	-	11.67	10.66
Biocrude Composition (wt%)								
C	-	-	75.81 (310°C) 77.25 (340°C)	75.77 (310°C) 76.46 (340°C)	-	-	-	-
H	-	-	8.67 (310°C) 8.77 (340°C)	8.90 (310°C) 8.88 (340°C)	-	-	-	-
O	-	-	10.16 (310°C) 8.95 (340°C)	10.21 (310°C) 9.78 (340°C)	-	-	-	-
N	-	-	5.36 (310°C) 5.03 (340°C)	5.13 (310°C) 4.88 (340°C)	-	-	-	-
S	-	-	-	-	-	-	-	-
Hydrochar Ca (mg/kg)^A	-	61740	-	-	-	-	-	-
Hydrochar Mg (mg/kg)^A	-	19040	-	-	-	-	-	-
Hydrochar P (mg/kg)^A	-	40230	-	-	-	-	-	-
Feedstock P (mg/kg)^A	-	12870	-	-	-	-	-	-

Note: ^A Dry-basis (db), ^B Dry and ash-free basis (daf), NS - not stated, only the predominant inorganic elements are mentioned.

Using chicken manure as a feedstock for HTL has not been extensively studied [49]. Furthermore, the studies found involving chicken and poultry manures have predominantly been conducted at the optimal conditions found for dairy and swine manures [2, 42, 49]. Due to the unique composition of chicken and poultry manures, these conditions may not necessarily be ideal. The results from all available literature found involving chicken and poultry manures have been summarised in Table 3 above.

In addition, the properties of chicken manure change over time due to the activity of volatile substances as well as due to microbial degradation [30, 31]. This results in varying optimal conditions for processing based on the age of manure among other factors. For example, studies on the HTL of 3-week-old swine manure saw an increase in protein content and decrease in lipid content, which ultimately led to an approximate 27% decrease in biocrude yield [30]. Additionally, all literature found dealing with chicken or poultry manures performed HTL tests at subcritical conditions which may not be optimum, as research has shown that greater HTL biocrude yields can be achieved at supercritical conditions [12]. Finally, it has also been determined that the highest biocrude yield is not necessarily associated with the highest oil HHV and quality with respect to biofuel application [50]. Overall, the processing of chicken manure via HTL is still relatively novel and as such significant optimisations can still be made to maximise quality biocrude yields.

The following sections discuss the distribution of products when using chicken and poultry manures for HTL, with an in-depth analysis on the suitability of the biocrude obtained as a biofuel.

Product Distribution

The distribution of products obtained when using chicken and poultry manures as feedstocks for HTL can be seen in Table 3 above and Figure 10 below. The general trend observed for all studies is that the aqueous product is dominant, followed by hydrochar, biocrude and finally the gaseous product. The yields obtained range from 40.5-55.5% aqueous product, 16.0-37.1% hydrochar, 9.20-17.7% biocrude and 6.90-11.5% gaseous products. All percentages are on a dry-weight basis of biomass fed.

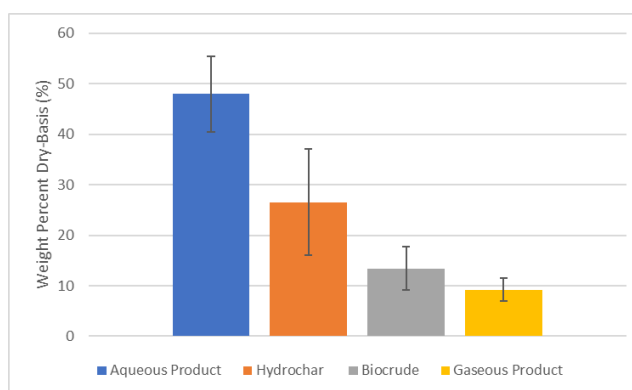


Figure 10: Bar graph showing the distribution of HTL products, on a dry-weight basis of biomass fed, when using chicken and poultry manures

Hydrochar

The chicken and poultry manure studies produced hydrochar yields of 16.0-37.1 wt% of the dry feed, with a HHV of 25.4 MJ/kg reported by Ekpo et al. [32] when using chicken manure. The hydrochar yields were significant due to the high inorganic content of chicken manure [37]. These results suggest that a significant portion of the feedstock is converted to hydrochar during HTL of chicken and poultry manures and that the energy content is improved in comparison to the raw feedstock, which was 18.1 MJ/kg according to Ekpo et al. [32]. The

hydrochar produced predominantly consists of the inorganics (ash) from the manure, minor quantities of unreacted feedstock as well as char formed during the process [30]. Significant research is being done on applications of hydrochar, with potential as an energy carrier, soil amendment, filler for industrial applications, precursor for functional carbon materials and also as a filtration media [22, 30, 34].



Figure 11: Showing the physical appearance of hydrochar following HTL [91]

Furthermore, Li et al. [2] found that the mobile heavy metal fractions found in chicken manure were transformed into more stable forms in the solid residue following HTL. This caused a significant decrease in ecological risk from high-moderate to moderate-low for most heavy metals due to their decreased bioavailability when compared to the feedstock [2]. HTL studies performed on laying hen and broiler manures determined that 75-90% of zinc (Zn), 71-98% copper (Cu), 71-99% lead (Pb) and 88-92% of cadmium (Cd) were relocated to the hydrochar and largely transformed into more stable, low-risk complexes [2]. This trend has also been observed with other livestock manures during HTL [8]. Furthermore, most of the calcium (Ca), magnesium (Mg), aluminium (Al), iron (Fe) and phosphorus (P) species migrated to the hydrochar [13, 32].

Gaseous Product

Table 4: Showing the distribution of gaseous products following HTL of laying hen and broiler manures at 310 and 340°C, respectively. Data obtained from [13].

	HTL Temperature (°C)	Carbon Dioxide (CO ₂) wt%	Methane (CH ₄) wt%	Hydrogen (H ₂) wt%
Laying Hen Manure	310	96.89	ND	3.11
	340	90.92	2.31	6.77
Broiler Manure	310	95.29	ND	4.71
	340	90.44	1.40	8.16

Note: ND – Not detected

As mentioned previously, the gaseous product was obtained in the smallest quantity among the studies performed on chicken and poultry manures. Furthermore, out of the studies found, only Lu et al. [13] reported the composition of the gaseous product obtained after HTL. These results are reported in Table 4 above. As can be seen, for both laying hen and broiler manures, carbon dioxide was the predominant component with a contribution of 90.44 to 96.89 wt% among the tests performed at 310°C and 340°C. Carbon dioxide was also observed as the dominant gas by Ekpo et al. [32] when using chicken manure with HTL. Carbon dioxide is formed through numerous routes including the water gas shift reaction and decarboxylation reactions [42]. Hydrogen is the second largest gas contributor with 3.11-8.16 wt%, with the higher temperature (340°C) favouring its formation. Lastly, methane contributes up to 2.31 wt% with the lower temperature (310°C) inhibiting its formation. Furthermore, it is also expected that nitrogen-containing compounds are present in the gaseous phase, such as NH₃, N₂O and NO₂, however these were not detected in the study by Lu et al. [13].

Research has been conducted into possible applications for the gaseous products formed. It has been proposed that the hydrogen formed could be used in the subsequent upgrading step for biocrude and that the carbon dioxide could be used in combination with the aqueous product for biomass, such as microalgae, growth and cultivation [9,11, 40].

Aqueous Phase

The dominant HTL by-product when using chicken or poultry manures is the aqueous phase. It contains predominantly water as well as organic compounds [34]. Experiments performed by Lu et al. [13] found that the major constituents of the aqueous phase for laying hen manure, excluding water, were 6.78% ketones and aldehydes, 5.26% alcohols and phenols and 56.26% nitrogen-containing compounds based on the peak areas in GC-MS analyses. Similarly, for broiler manure, the aqueous phase contained 0.40% acids, 2.15% ketones and aldehydes, 2.70% alcohols and phenols and 66.68% nitrogen-containing compounds [13]. Ammonia was found to be the dominant nitrogen-containing compound, constituting approximately 75 wt%, whereas the remainder consisted of organics such as pyrazine and pyridine derivatives [32]. Moreover, when using chicken manure, it has been found that nearly all nitrogen, potassium and chlorine is found in the aqueous product after HTL [32].

Due to the high levels of organic nutrients, the aqueous product has been investigated for several applications. Anaerobic digestion (AD), supercritical water gasification (SCWG), biomass cultivation (e.g. microalgae for biofuel production or lipid extraction) and use in a microbial electrolysis cells have all been demonstrated as feasible methods to utilise nutrients in the aqueous phase and also produce valuable biogases (AD and SCWG) [9, 13]. Overall, it cannot be directly discharged due to the high total organic content (TOC) and especially due to the significant presence of harmful nitrogen-containing compounds [11, 13].

1. Biocrude Analysis

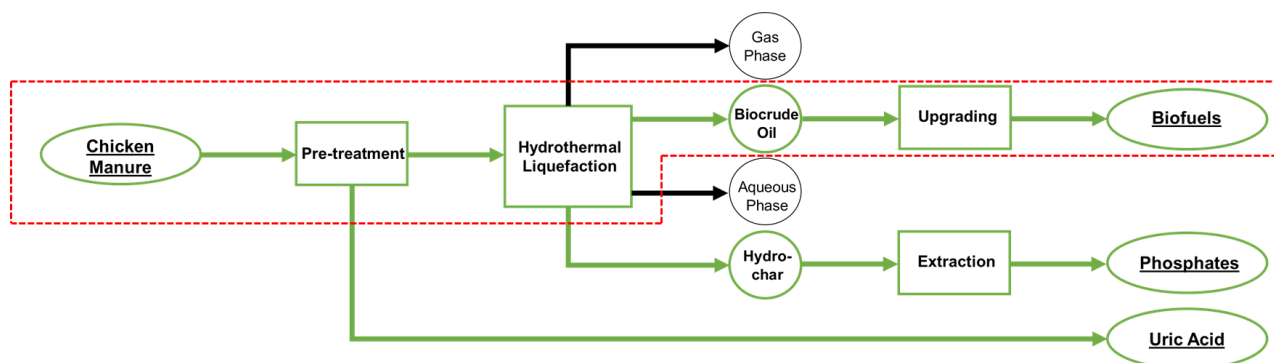


Figure 12: Showing the aspect of the biorefinery in focus for the biocrude analysis (indicated by red-dotted line)

The biocrudes obtained from HTL are semi-fluid, dark, viscous and have a smoke-like smell [48]. Midgett et al. [37] achieved the highest biocrude yield of 17.7 wt% using poultry manure at 350°C, 20.5 MPa, 15 minutes retention time, 1g Na₂CO₃ catalyst, 20 wt% (solids) feed, carbon monoxide (CO) as a process gas, 200 RPM agitation and a heating rate of 10°C/min. A similar yield, at 17 wt%, was achieved when using chicken manure by Ekpo et al. [32]; at the same temperature and similar pressure without the use of a catalyst or process gas. This suggests that near critical conditions (374°C) could be best for the processing of chicken manure. However, Lu et al. [13] and Ni et al. [39] observed a decrease in biocrude yield when increasing the processing temperature from 310 to 340°C, which could be due to differences in heating rate and retention time applied, among other parameters, in comparison to the two tests mentioned above. As seen in Table 3, the tests performed involve varying operating

conditions and thus no definitive conclusion can be made as to the optimal processing parameters and biocrude yield. Nonetheless, a yield of more than 17 wt% of the dry feed is significant, especially when considering that the tests were not performed at optimal conditions or on a continuous basis and furthermore that chickens produce enormous amounts of manure annually [52].

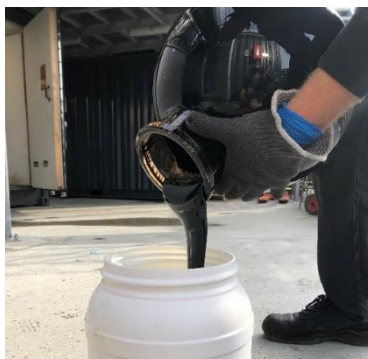


Figure 13: Showing the physical appearance of biocrude following HTL [92]

The quality of the biocrude obtained is commonly assessed based on HHV, among other parameters [11, 48]. It is defined as the amount of energy released upon combustion when starting at 25°C and allowing the products to return to 25°C, while also including the latent heat of vaporisation of water within the products [53]. It is thus a representation of the energy content of the fuel but furthermore gives an indication of the oxygen, nitrogen, hydrogen and carbon content [48]. The studies summarised in Table 3 produced biocrude products with HHV values ranging from 32-37 MJ/kg which shows a significant improvement from the values deduced for the respective feedstocks (10.7 -18.1 MJ/kg). This proves that chicken manure can be successfully and readily processed using HTL to produce an energy-dense fuel [30, 42]. Lastly, it is advantageous to produce biofuels with similar HHVs to conventional fuels as it minimises engine modifications required and thus determines ease of implementation [48]. This is taken into consideration in the subsequent section, where the suitability of the biocrude obtained as a biofuel is analysed in detail.

Biocrude Composition and Comparison to Modern-day Fuels

Among the tests found using chicken and poultry manures, the only study that conducted thorough analysis on the content of the biocrude formed was by Lu et al. [13]. Using GC-MS, it was found that the biocrude contained a wide range of compounds with no dominant class [13]. It was found that for laying hen manure, the biocrude consisted of 7.08% hydrocarbons, 34.1% acids and esters, 30.7% alcohols and phenols, 6.65% ketones and aldehydes as well as 16.7% nitrogen-containing compounds based on the peak areas of the compounds constituting these groups. Similarly, for broiler manure, the biocrude consisted of 6.63% hydrocarbons, 48.8% acids and esters, 21.3% alcohols and phenols, 3.22% ketones and aldehydes as well as 14.2% nitrogen-containing compounds. These results were grouped together as chicken manure and can be seen in Figure 14 below.

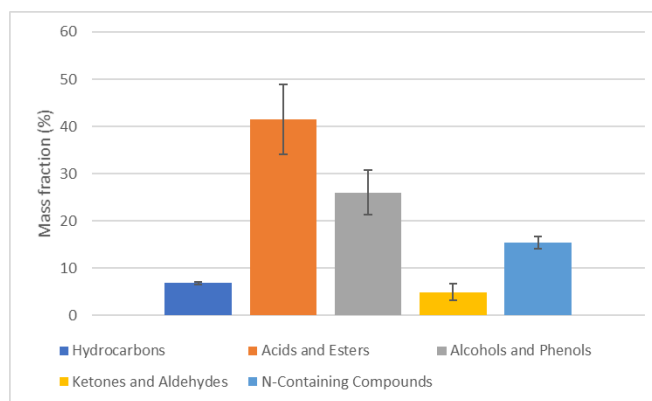


Figure 14: Bar graph showing the distribution of components in the biocrude following HTL of laying hen and broiler manures (grouped together as chicken manure). Data is based on GC-MS results from [13]

The acids and esters present were predominantly long-chain compounds (C16-27) and the aldehydes and ketones were all chain compounds [13]. The hydrocarbons and nitrogen-containing compounds were in the forms of chain and cyclic compounds [13].

For laying hen manure, the major compounds present were vaccenic acid (11.5%), hexadecanoic acid derivatives (14.3%), phenol and its derivatives (30.7%) and $C_{25}H_{29}NO_3$ (9.24%) based on the GC-MS results. For broiler manure, the major compounds present were heptadecyl acetate (19.9%), hexadecanoic acid derivatives (21.4%) as well as phenol and its derivatives (21.3%). However, due to the complex nature of the biocrude and the different properties of the constituents, total speciation is difficult [55]. This complexity prevents effective chromatographic separation which results in broad signals and as such limits the accuracy of GC-MS analyses [48]. Thus, further FTIR analysis showed that the main functional groups present in the biocrude were indicative of alcohols, acids, ketones, hydrocarbons and nitrogen-containing compounds [13]. FT-ICR MS also identified N1O1, N2 and N2O1 nitrogen species as dominant in the biocrudes obtained, while GC-MS results indicated that long chain amides, dibenzylamine, N,N-dimethyldodecanamide as well as other polycyclic structures were dominant [13, 39]. These nitrogen compounds are present as a result of protein degradation during HTL as well as from the reactions of other nitrogen-containing compounds in the raw manure [9]. Additionally, the main oxygen-containing compounds in the biocrude are organic acids, ketones, phenols, alcohols and aldehydes [48]

Furthermore, Lu et al. [13] also analysed the elemental composition of the biocrudes obtained when using laying hen and broiler manures, respectively, at both 310 and 340°C. These results, along with the elemental composition of the raw feedstocks and a few modern-day fuels, are summarised in Table 5 below. The HHV values for raw manures and biocrudes from Table 3 are also indicated along with the HHV values for the modern-day fuels. The laying hen and broiler manures were grouped as 'Raw Chicken Manure' and the biocrudes obtained at 310 and 340°C for both manures were labelled collectively as 'Biocrude'.

Table 5: Showing a summarised elemental and HHV comparison between raw manures, biocrudes obtained and some modern-day fuels [13, 93-95]

	Raw Chicken Manure	Biocrude	Crude oil	Diesel	Gasoline	Biodiesel
% C	45.7 – 53.2	75.8 – 77.3	82.0 – 87.0	83.0 – 87.0	83.0 – 87.0	77.0 – 80.0
% H	5.80 – 6.70	8.70 – 8.90	11.0 – 14.0	10.0 – 14.0	10.0 – 14.0	10.0 – 12.0
% O	22.4 – 33.4	9.00 – 10.2	0.1 – 4.00	NG	0.10 – 1.50	8.00 – 12.0
% N	3.70 – 4.50	4.90 – 5.40	0.1 – 2.00	NG	0.10 – 2.00	0.00 – 1.50
% S	NG	NG	0.1 – 6.00	< 0.05	< 1.00	NG
HHV (MJ/Kg)	10.7 – 18.1	30.0 – 37.0	42.0 – 47.0	42.0 – 46.0	44.0 – 46.0	39.0 – 41.0

Note: NG - negligible

The oxygen content of the starting manures was given based on typical values as it was not stated by Lu et al. [13]. Overall, the oxygen component of the biocrude was significantly reduced (more than double) in comparison to the raw manures. This occurs predominantly through dehydration (removed as water) and decarboxylation (removed as carbon dioxide) reactions occurring during HTL [54]. Furthermore, the nitrogen fraction of the biocrude increased slightly in comparison to the starting manure. As can be seen in Table 5, the oxygen and nitrogen contents of the biocrude are higher than that in diesel and gasoline while the carbon and hydrogen contents are lower. Additionally, with regards to biodiesel, the hydrogen content is lower, nitrogen content is higher, oxygen content is suitable and the carbon content is slightly lower. This analysis shows that the elemental composition of the biocrude resembles biodiesel to the greatest extent but overall is largely incompatible with these modern-day fuels.

Conventional fuels such as diesel and gasoline are principally comprised of aliphatic and aromatic compounds, whereas kerosene (jet fuel) contains primarily paraffins and aliphatics [9, 37]. As mentioned previously, GC-MS results indicate that the biocrude contains few hydrocarbons (< 7.2%) and no dominant class of compounds. This trend was further confirmed by Midgett et al. [37] when using poultry manure. The aliphatic compounds present in the biocrude include cyclic, straight and branched compounds but insignificant amounts of C5-10 and C10-20 alkanes which are the major components of gasoline and diesel respectively [9, 37]. The biocrude also contains insignificant amounts of alkenes which are found in diesel but does contain a considerable amount (> 34%) of long-chain fatty acid esters that are dominant in biodiesel [13]. Furthermore, the HHVs of the biocrudes obtained are lower in comparison to these modern-day fuels, as seen in Table 5, and the viscosities are generally 10-10000 times higher depending on feedstock and operating conditions [48].

Overall, the physical and chemical properties of biocrude obtained when using chicken or poultry manures fall short of fuel standards. This makes it unsuitable to use directly as a drop-in replacement for gasoline, diesel and to a lesser extent biodiesel.

Applications of Biocrude

It has been proven that the biocrudes produced by HTL can be used directly as a fuel for burners, boilers, turbines as well as in heavy engines such as for marine applications [11, 12, 44, 48]. Additionally, depending on the biocrude properties and most notably nitrogen content, it can potentially be used directly as a blend with conventional fuels such as diesel (<5 wt%)

[48, 59]. However, the blend is predominantly fossil fuel and coking and corrosion issues pose limitations [48, 59].

Despite these applications, the use of biocrude as a replacement for gasoline, diesel, jet-fuel or biodiesel would prove vastly more advantageous due to the integrated nature of these fuels in current society. As discussed previously, the biocrude obtained from chicken or poultry manures has properties that do not comply with conventional fuel standards [48]. In summary, the compositions differ significantly and the high oxygen and nitrogen content renders biocrude unstable for storage (polymerisation and degradation of components occurs), decreases HHV, leads to catalyst deactivation in subsequent uses, causes corrosion and coke formation as well as the emission of NO_x when combusted [11, 13, 48]. Furthermore, the viscosity and HHV of biocrudes obtained do not comply and the vapour pressure and cetane number, an indication of ignition quality, may not be appropriate due to the unsuitable content of the biocrude [48].

Biocrude Upgrading

Due to these limitations, biocrude can be optimised through upgrading in order to meet modern-day fuel standards [44]. Upgrading involves the removal of heteroatoms, hydrocarbon saturation, cracking and other mechanisms in order to improve physical and chemical properties [11, 48]. It is considered a required complement to the HTL process for industrial realisation and can be achieved using existing refinery technology [11, 12]. Current available methods of biocrude extraction and upgrading are discussed in detail below.

Prior to upgrading, the biocrude needs to be isolated from the rest of the products. On a lab scale this is commonly performed gravimetrically followed by solvent extraction [46, 55]. In HTL studies the biocrude is generally extracted using polar solvents such as acetone, ethanol, tetrahydrofuran and dichloromethane; with the choice of solvent depending on the biocrude composition [48]. Additionally, more than one solvent can be used to fractionate the oil product and increase the amount of biocrude extracted because solvents are selective towards certain compounds [2,48]. Distillation is another method that can be used to separate the biocrude product and also enhance its properties through fractionation [48]. This method is not commonly adopted on lab scale as it is not necessary to analyse the biocrude, however it is the method most likely to be used on an industrial scale [48]. There are several options available including fractional distillation, vacuum distillation and steam distillation [48]. Vacuum distillation is attractive as it allows for separation at lower temperatures, thus minimising degradation of the biocrude components [48].

Once the biocrude is extracted, it can subsequently be upgraded. Information on biocrude upgrading following HTL is scarce, with most information based on the upgrading of bio-oils following pyrolysis, which is ultimately based on petroleum refining techniques [48]. Additionally, fuel specification analyses and engine tests of upgraded biofuels from HTL are limited due to the small quantities of biocrude produced on a lab scale, and thus their feasibility as alternative transportation fuels remains largely undetermined [59]. Furthermore, there was no literature found dealing with the upgrading of biocrude derived from chicken manure; with only a few studies dealing with the upgrading of livestock manures in general [48].

Upgrading results in the modification of biocrude properties such as HHV, density, viscosity, chemical composition and vapour pressure in order to meet those of fuel standards [48]. It is essential to characterise the biocrude thoroughly prior to upgrading because the oxygen, nitrogen as well as inorganic content determine which treatment and conditions are most efficient and effective [11,13]. Currently, there are several promising methods available for biocrude upgrading including: the use of hydrogen-donor solvents, hydrotreating, catalytic

hydrocracking, esterification, steam reforming and hybrid processes. These are discussed in detail below.

Hydrogen-donor Solvents

Hydrogen-donor solvents have been discussed previously as additions during HTL, however they can also be implemented after. The addition of hydrogen-donor solvents such as tetralin, ethanol and methanol have been found to improve stability of the biocrude, as they arrest free-radical polymerisation and subsequently prepare it for further upgrading processes [48, 56]. Moreover, these solvents can also reduce viscosity of the biocrude which makes it easier to process and more suitable as a fuel [56].

Hydrotreating

Hydrotreating is commonly implemented in upgrading and involves the reaction of organic compounds with hydrogen at high pressures (10-20 MPa), moderate temperatures (250-450°C) and in the presence of a catalyst [48, 56]. The treatment results in hydrocarbon saturation through hydrogenation as well as the removal of oxygen in the form of water and carbon dioxide, nitrogen in the form of ammonia and sulphur in the form of hydrogen sulphide [48, 56]. This improves the stability and quality of the biocrude by reducing reactive components and altering the chemical composition to attain fuel standards [56]. The catalysts used are commonly cobalt-molybdenum (CoMo), nickel-based, alumina-based and noble metals among other metals [56]. The choice of catalyst is pivotal as deactivation should be avoided and furthermore different catalysts favour the formation of different fuel standard compositions. For example, sulphide-CoMo catalysts show less saturation of aromatic compounds which is desired for gasoline [48]. Hydrotreating has proven effective in upgrading biocrude derived from plant feedstocks (such as corn stover, duckweed and hardwood), by removing oxygen and to a lesser extent nitrogen, improving HHV as well as improving saturation [48]. However, several studies have noted that hydrotreating of biocrude results in low yields of upgraded biocrude, catalyst deactivation and the extreme conditions employed have resulted in the undesirable formation of coke [11, 48, 59]. Due to this, hydrotreating under milder conditions is often implemented prior to the extreme conditions [48]. This improves biocrude stability and limits char formation during extreme conditions, which ultimately improves upgraded biocrude yields [48]. Lastly, it has been found that higher product quality results in lower yields, which implies that the optimal compromise must be determined in order to maximise the feasibility of hydrotreating [56].

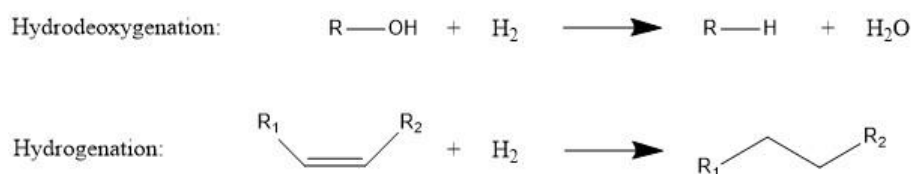


Figure 15: Showing two possible reactions occurring during hydrotreating. Hydrodeoxygenation shows the removal of oxygen in the form of water and hydrogenation shows the saturation of an alkene. Both reactions require a catalyst. Adapted from [48].

Catalytic Hydrocracking

Catalytic hydrocracking is deemed the most suitable cracking method, among thermal and zeolite cracking, due to the milder reaction conditions and greater compatibility with HTL biocrude [48]. Catalytic hydrocracking involves the cracking of complex components of the biocrude, in the presence of hydrogen, into simpler molecules matching those found in conventional fuels [56]. During cracking, reactions such as dehydration, decarboxylation,

dehydrogenation and hydrogenation occur to produce desired products [48]. It involves moderate to high temperatures (>350°C), high hydrogen pressures (>15 MPa) as well as the presence of a catalyst [56]. Commonly used catalysts are natural clays and alumina-based catalysts [48]. The combination of hydrotreating followed by hydrocracking is an attractive option for biocrude upgrading, whereby the remaining undesired heavy components after hydrotreating can be cracked [48]. However, as with hydrotreating, the harsh conditions employed can result in coke formation and moreover economic limitations due to the high costs involved [56].



Figure 16: Showing a possible hydrocracking reaction, which requires the presence of a catalyst [48].

Esterification

Esterification is an attractive process to produce biodiesel standard fuel from biocrude owing to its simplicity, mild operating conditions and low-cost reactants [56]. The primary reaction of focus is between organic acids and an alcohol, usually methanol due to its low cost, to produce alkyl esters which are found in biodiesel [48, 56]. Furthermore HHV, viscosity, density, aging rate as well as water and oxygen content have been proven to improve whereas the nitrogen content does not [48, 56].



Figure 17: Showing a possible esterification reaction, where a carboxylic acid is converted to an ester along with the formation of water [48].

Chen et al. [60] published the only paper found evaluating the fuel specifications and engine performance of upgraded HTL biocrudes. They combined distillation and esterification, following the HTL of swine manure, to effectively produce an upgraded fuel that meets biodiesel standards and as such can be used as a diesel blendstock [60]. It was concluded that hydrotreating was not required in order to produce drop-in biofuels from wet biomass [60]. Furthermore, Chen et al. [60] stated that HTL integrated with distillation and esterification yields a higher energy recovery ratio (energy of upgraded biofuel/energy of raw feedstock) at 0.8 compared to HTL in combination with hydrotreating at around 0.3. HTL in combination with distillation and esterification also showed a lower energy consumption ratio (energy required to produce upgraded biofuel/energy released by biofuel upon combustion) at 0.03-0.06 compared to 0.24 for HTL followed by hydrotreating [60]. The success in upgrading biocrude from swine manure is a promising achievement as Li et al. [2] found that the biocrude obtained from swine, laying hen and broiler manures had similar chemical compositions.

Supercritical Operations and Steam Reforming

Moreover, performing esterification at supercritical conditions has received increasing attention as it has proven to drastically improve the HHV, acid number (indication of acid content) as well as decrease the viscosity, oxygen and nitrogen content of pyrolysis bio-oils [56]. Additionally, steam reforming is another upgrading technique that has been extensively studied on pyrolysis bio-oils, but not HTL biocrude [59]. It involves the production of a

synthesis gas as a renewable fuel using high temperature steam in the presence of a catalyst [56, 59].

Hybrid Processes

Finally, different features from available upgrading processes can be combined in order to maximise the benefits of each technique and overcome their respective limitations [48]. This was effectively performed by Chen et al. [60], in the aforementioned study, and has also been successfully achieved when using other plant-derived feedstocks [58].

Overall, it should be mentioned that very few studies accomplished significant nitrogen reduction during the upgrading of biocrudes [61]. Successful studies include continuous upgrading processes, operating at extreme conditions, which achieved almost complete nitrogen removal [61]. The results discussed suggest that the production of diesel blendstocks may be the most promising route for the upgrading of chicken manure biocrude; as it can be achieved relatively cheaply and the resilient nitrogen content could be diluted to an acceptable extent [59]. However, the selective removal of these nitrogen-containing compounds should be investigated further as it would prove vastly beneficial in aiding the modification of biocrude to modern-day fuels. In conclusion, further experiments should be conducted in order to first determine the optimal HTL processing conditions of chicken manure, after which the most effective and feasible upgrading procedure can be assessed.

Associated Costs and Emissions with HTL Operations

There have been several studies published performing techno-economic analyses on a variety of feedstocks for HTL, however information on chicken manure is limited. A recent paper by Bora et al. [34] investigated HTL in combination with upgrading to produce petroleum fuels, using poultry manure, and concluded that the major contributors to equipment costs are the HTL reactor ($\approx 25\%$) and upgrading processes ($\approx 20\%$). Furthermore, it was calculated that this integrated system would emit approximately 94.5 g CO₂-eq/kWh provided by the upgraded biofuel [34]. The calculation for this can be seen in Appendix part 1. This is significantly lower than that for conventional fossil fuels such as coal (955 g CO₂-eq/kWh), crude-oil (818 g CO₂-eq/kWh) and natural gas (446 g CO₂-eq/kWh) [45]. This significant reduction in carbon dioxide emissions is also expected for chicken manure, due to its correlation with poultry manure, and was further supported by Tzanetis et al. [62] and de Jong et al. [63] where they achieved an 85% and 77-80% CO₂ reductions, respectively, in producing a bio-jet fuel.

Tzanetis et al. [62] determined, at the time and place of the HTL study, that the associated costs of bio-jet fuel production are twice as high as for the fossil fuel alternative when using forest residues. Zhu et al. [64] determined the minimum fuel selling price (MFSP) for upgraded HTL biocrude derived from woody biomass, using current state of the art technology, to be \$4.44/gallon gasoline equivalent (GGE); which was 1.5 times higher than the average gasoline price at the time [64]. The same study determined that process improvements in the future as well as the establishment of mature HTL technologies could reduce the price to \$2.52/ GGE, which is an almost 40% reduction in costs making it highly competitive with gasoline. Similar to Zhu et al. [64], Snowden-Swan et al. [65] concluded that the MFSP for upgraded HTL biocrude when using sludge waste is \$4.90/GGE. Furthermore, Pedersen et al. [66] determined a MFSP for upgraded woody biocrude to be on average almost two times the price of the fossil fuel equivalent, while Nie and Bi [67] had a similar conclusion at 63-80% higher costs when using forest residues. Overall, all feasibility studies show a similar production price in comparison to their fossil fuel counterparts, at approximately 1.5-2 times the price.

In the studies assessed, the feedstock price and product yields were found to affect the final product price most significantly, followed by upgrading costs and reactor operating

requirements [48, 66]. The cost of chicken manure is approximately \$15-40/tonne whereas the feasibility studies investigated above have values ranging between \$3-95/tonne raw feedstock, with most in the middle range showing comparable values to chicken manure [31, 62, 64-67, 80]. The cost of producing upgraded biocrude from chicken manure cannot be deduced because despite the relatively similar feedstock costs, the product yields vary and upgrading requirements differ due to the dissimilar compositions of the biocrudes obtained.

Overall, all studies concluded that current technology does not give an economically competitive biofuel product compared to fossil fuels, which almost certainly also applies to the use of chicken manure as a feedstock. However, most studies proved that the MFSP of HTL biofuels is competitive with other renewable technologies such as pyrolysis, which highlights its promise as an alternative energy-provision method [11]. Furthermore, with erratic petroleum prices, new developments in HTL operations as well as potential government support; HTL processing could prove economically viable in the near future [37, 41, 42].

Suitability of the Biocrude as Biofuel Conclusion

Based on the analysis completed, chicken manure can be effectively used as a feedstock for HTL to produce an energy-rich fuel, with yields of greater than 17 wt% (dry basis). Studies produced biocrude products with HHV values ranging from 32.0-37.0 MJ/kg which shows a significant improvement from the values deduced for the respective feedstocks (10.7-18.1 MJ/kg). Furthermore, these studies were not performed at experimentally determined optimal conditions or on a continuous basis, which would further improved yields [11, 51].

Despite the production of an energy-rich fuel, the composition of the biocrude obtained needs to be altered in order to achieve fuel standards. The success of upgrading biocrude obtained from chicken manure is uncertain due to literature limitations, however the upgrading of other HTL biocrudes have proven successful. The most relevant of which produced biodiesel standard fuel from swine manure by relatively straightforward as well as cost and energy-effective distillation followed by esterification. This is a promising result as swine manure produces a similar biocrude to chicken manure [2].

Additionally, the costs associated with HTL and upgrading of various feedstocks have proven to be economically uncompetitive with fossil fuels, which almost certainly also applies to the use of chicken manure. However, the costs associated proved comparable to other biofuel technologies, which is a promising indication of its future success. Additionally, upgraded biofuels produced from chicken manure also show great promise because the carbon dioxide emissions associated with the process are expected to be significantly reduced in comparison to fossil fuels. Moreover, it has been proven that HTL when using chicken manure significantly stabilises heavy metals, destroys antibiotic resistance genes, kills pathogens, removes odorous compounds and has possible applications for all the by-products produced [2, 9,11,12]. These factors highlight the prospects and possibilities of using HTL with chicken manure to produce biofuels. Overall, the results analysed prove that HTL of chicken manure, in combination with upgrading, has great potential in producing functional biofuels, with significant optimisations for this process still possible.

However, due to the limitations scope of this analysis, it is imperative that laboratory testing is performed in order to reach definitive conclusions. It is recommended that the optimal HTL and upgrading conditions for processing chicken manure be investigated. This will allow for a more accurate conclusion as to the feasibility and competitiveness of the final biofuel product. Additionally, continuous processing of chicken manure with HTL and upgrading should also be tested, as it is required for industrial application and previous studies have achieved improved results [11]. Lastly, further studies should be conducted on the potential use of

hydrogen gas generated during HTL for upgrading, the selective extraction of nitrogen-containing compounds from the biocrude, the co-processing of biocrude and crude oil in petroleum refineries as well as the use of novel methods such as extracting proteins prior to HTL in order to reduce nitrogen content in the biocrude [11].

2. Uric Acid Analysis

Overview

Uric acid (UA) is the most abundant nitrogen compound in fresh chicken manure, constituting around 20% of the total nitrogen [68, 69]. Uric acid content ranges from 15-57 kg/tonne of chicken manure which translates to a worth of approximately \$180-684/tonne of chicken manure [31, 68, 71]. The calculation for this can be seen in Appendix part 2. This result indicates the significant monetary value of uric acid present in chicken manure, especially when considering the enormous quantities of manure produced.

The uric acid content of chicken manure can vary significantly with species, diet, the waste management system implemented and especially with time [31]. Chickens fed a high-protein diet can have approximately three times higher uric acid in their manures than chickens on a low-plane nutrition [31]. The amount of uric acid present in the manure is also significantly dependent on time, as uric acid is microbially degraded by widespread enzymes which results in the production of ammonia [31, 68, 69]. This degradation is aided by high temperatures and moisture [31, 68]. Uric acid is mineralised relatively rapidly to ammonia through allantoin, allantoinic acid, ureidoglycolate followed by urea [69]. The reaction looks as follows:

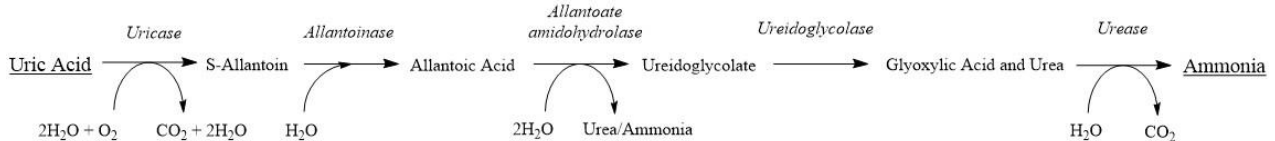


Figure 18: Showing the enzyme-mediated degradation of uric acid to ammonia. The enzymes involved are written in italics. Adapted from [97].

Based on the studies where chicken and poultry manure HTL products were chemically analysed, there was no indication of uric acid in any of the products [9, 13, 32]. Additionally, during HTL of these manures at least 40% of the nitrogen in the feedstock migrated to the aqueous phase product, of which more than 75% was ammonia. These factors indicate that hydrothermal conditions most likely resulted in the degradation of uric acid to ammonia. Literature further supports this, as it has been reported that oxidative decomposition occurs at 250°C for uric acid [20, 72]. The absence of appreciable amounts of uric acid in any of the HTL products suggests that it should be extracted prior to HTL.

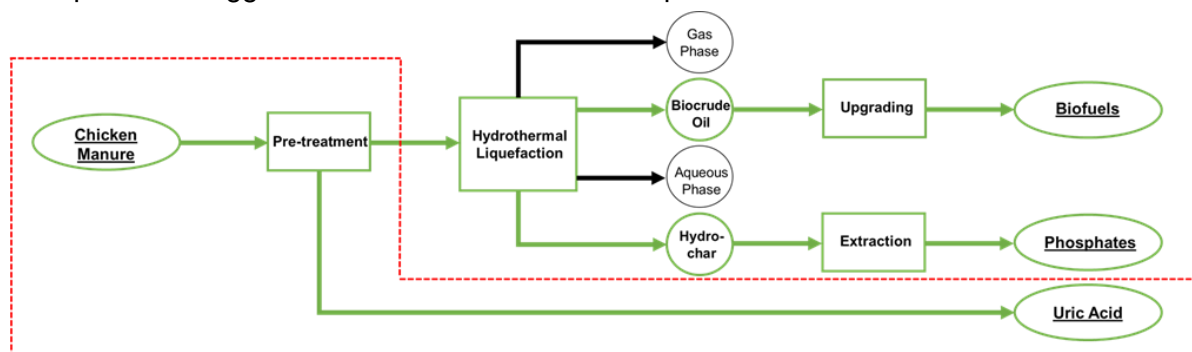


Figure 19: Showing the aspect of the biorefinery in focus for the uric acid analysis (indicated by red-dotted line)

It is largely accepted that uric acid degrades over time especially with an increased presence of moisture [31, 68, 69]. Gross et al. [71] found that after 14 days virtually all uric acid from chicken manure was degraded and similarly, Douros and Warder [20] found that after 8 days there was negligible uric acid remaining. Despite the decrease recorded by many studies, Mowrer et al. [69] reported a substantial increase in uric acid over the first 8 days after aerated incubated at 30°C with moisture present. Day 6 saw the highest uric acid levels relative to day 0, at an average of approximately 70% higher over the tested samples. However, after day 8 the concentration with respect to day 0 declined as expected. This increase was proposed to be due to the catabolism of guanine and adenine nucleotides present [69]. These results indicate that in order to maximise the extraction of uric acid, further tests should be conducted analysing its behaviour over time.

Furthermore, the waste management system implemented also has an influence on the presence of uric acid [70]. Strategies such as using wooden slats or inducing air movement to reduce moisture have shown to affectively reduce microbial degradation [31]. Additionally, the use of mineral acids such as formalin, sulfuric acid and hydrochloric acid have proven to inhibit bacterial activity for 5-14 days [31]. These factors should also be considered in order to optimise uric acid levels for extraction.

Uric acid extraction from chicken manure in combination with HTL is a novel procedure, with no open publications found relating to the topic. Furthermore, there are only few publications available involving the extraction of uric acid from chicken manure and they are in the form of patents that were released prior to 1984. Overall, one of the main challenges associated with uric acid extraction from chicken manure is the removal of resilient, coloured contaminants [20, 72, 73].

Regarding the biorefinery in question, two of the most promising extraction methods found for chicken manure, that overcome the pigmentation problem, as well as their potential compatibility with HTL are summarised and discussed below.

1. United States Patent 4007186 - Emanuel, deceased et al – Feb 8 1977 [72]

This patent involves a multi-stage process for the extraction and preparation of uric acid of varying degrees of purity. It is an attractive technique due to this versatility, claimed high yields and also because it particularly targets extraction from chicken faeces which is pertinent to this research task. A flow diagram of the general procedure can be seen in Figure 20 below.

The process involves phase one, where uric acid of 80-90% purity is obtained by dissolving the faecal matter in a dilute alkali solution after which the undissolved solids are removed. Dissolution is preferably achieved through rigorous mixing under inert atmosphere and by using 2-5% triethylamine solution, but other basic salts such as KOH or primary to tertiary organic amines can be used. Uric acid as well as other soluble materials are extracted into solution while the majority of solid residue remains in suspension. The liquid and solid phase are then separated by means such as centrifugation or filtration. By adding excess ammonia salts, such as diammonium hydrogen phosphate, to the liquid phase; ammonium urate is precipitated and subsequently separated, washed and dried. Ammonium urate can then be readily converted to uric acid, by conventional methods, to the desired 80-90% purity.

Uric acid of improved purity can be prepared in phase two, where the ammonium urate obtained in phase one is dissolved in another dilute alkaline solution. By using a dilute mineral acid such as hydrochloric acid, the alkaline solution is then gradually adjusted to a pH of about 10.5 to precipitate urate salt which is readily filtered. The washed and dried urate salt is further suspended in a hot dilute mineral acid, such as perchloric acid, which converts the urate salt

to a uric acid precipitate. This precipitate is then washed and dried to obtain a uric acid product of around 99% purity, which is useful for synthesising other chemicals.

Furthermore, there is a third phase where crystalline uric acid of very high purity can be achieved to serve as a reference standard. This is performed by dissolving the product obtained in phase one or two in a hot perchloric acid solution, after which the solution is cooled gradually, forming perchlorate salt crystals containing uric acid. The perchlorate salt crystals are then filtered off, dried and dissolved in a second hot perchloric acid solution after which the same procedure of cooling, filtration and drying of perchlorate salt crystals occurs. These crystals are then suspended in warm water to dissolve perchloric acid and precipitate uric acid crystals. The uric acid crystals are then filtered, after which it is advised to wash with distilled water and subsequently dry with anhydrous, distilled methanol. This process results in a crystalline uric acid purity of approximately 99.9% with no pigmentation. In addition, highly crystalline 99.9% uric acid can be obtained by further dissolving the 99.9% uric acid product or the second batch of perchlorate salt crystals in a sodium hydroxide solution. Perchloric acid is then added, after which the solution is cooled, resulting in a uric acid precipitate which is consequently filtered off, washed and dried to give large crystals of ultra-pure 99.9% uric acid.

The unused solid residues produced after phase one have feed and supplement value, which suggests they are likely viable feed for HTL to produce biocrude [72]. Furthermore, the solid residue removed in phase two, as seen in Figure 20, may also prove to be usable HTL feed. However, this needs to be investigated further in order to determine the compatibility of the residues with HTL, taking into account the amount of uric acid extracted, the biocrude quantity and quality obtained and as such the overall feasibility of the method.

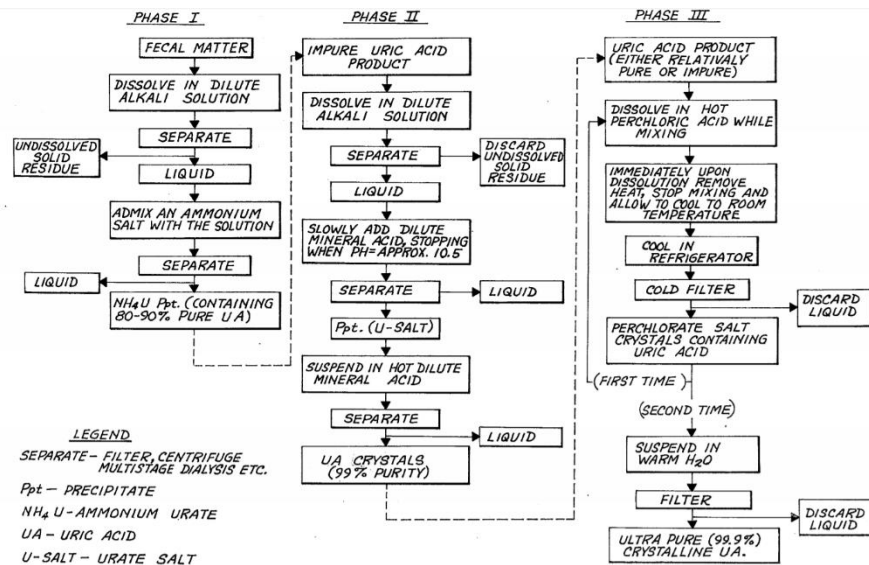


Figure 20: Flow diagram from US Patent 4007186 showing the procedure for uric acid extraction [72]

2. United States Patent 4045582 - Douros, Jr. et al. – Aug 30 1977 [20]

This patent relates to fowl excrement and is as such well suited to chicken manure. This procedure is attractive as it can be implemented on a continuous large-scale basis and it produces high purity uric acid or uric acid primary salts which are of chemical and pharmaceutical grade. Furthermore, it only treats less than 40% of the raw dry manure with chemicals, thus leaving a large fraction viable as a feedstock for HTL. A flow diagram of the general procedure can be seen in Figure 21 below.

The procedure involves an initial drying step to terminate biological degradation of UA, followed by grinding and fractioning according to particle size. This results in smaller sieved fractions, < 80 openings/in² mesh, with usually more than 70% of all uric acid. This drastically cuts down on the amount of material which must be handled in subsequent steps.

The fraction with higher uric acid content is then dissolved in an aqueous alkaline-brine solution, which can be any organic or inorganic material which gives a pH of preferably greater than 9 and has a cation to form a salt with uric acid. Sodium, lithium and potassium hydroxides are preferred. The solid impurities are then filtered or centrifuged after which a flocculating agent such as calcium chloride is added. This forms a slurry containing other insoluble impurities which are subsequently removed. At this stage, a majority of the undesired raw material has been removed. A sufficient amount of acid is then added to the resulting solution to form uric acid precipitate. This acid can be any material that when added to the solution lowers the pH to around 6 and is preferably a mineral acid such as hydrochloric or sulphuric. Thereafter, this precipitate is removed by filtration or centrifugation and is extracted with an aqueous alkaline solution. Another similar acidic solution is then added to form a substantially pure uric acid precipitate.

If the uric acid at this point is not largely white, the last alkaline solution can be heating and passed through a carbon-containing material, such as activated carbon, to remove colour impurities. The carbon material is then removed, and the acidic solution is added to form uric acid precipitate. The precipitate is then washed with an aqueous solution followed by an inert liquid, that does not solubilise the uric acid, and is then finally dried. This process yields generally 90-95% of the uric acid in the concentrated fraction (<80 mesh). The product is of chemical grade and is readily adaptable for pharmaceutical purposes. The process can produce substantially pure uric acid or uric acid primary salts (98-99.8% purity) depending on the pH adjustments made and the alkaline solution used.

The unused residues following grinding and sieving have feed and supplement value and thus are most likely compatible with HTL to produce biocrude. Furthermore, insoluble material is removed at two later stages, as seen in Figure 21, which may also prove to be viable HTL feed. However, the drying step required for this process may impose further economic limitations to HTL operation, because the ability to process wet feedstock reduces operational costs significantly. To determine the compatibility of this method with HTL, studies should be conducted with the removed residues in order to assess the amount of uric acid obtained as well as the quality and quantity of biocrude produced.

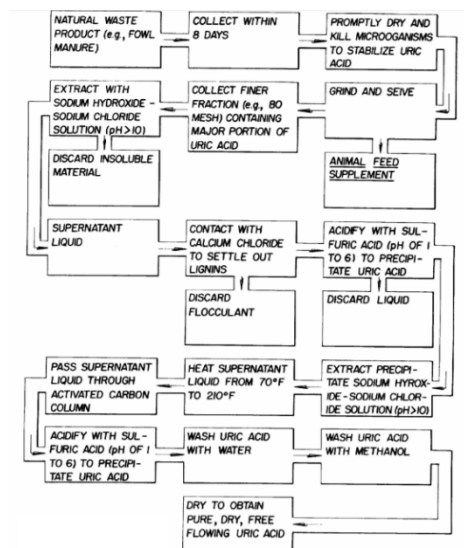


Figure 21: Flow diagram from US Patent 4045582 showing the procedure for uric acid extraction [20]

Conclusion and Recommendations

Based on the analysis completed, uric acid must be extracted prior to HTL, as it is decomposed under HTL conditions. The viability of this extraction cannot be concluded because no experimental studies were found on this topic. However, both procedures described above produce large quantities of residue in the early stages which are relatively unprocessed and of nutritional value, suggesting that they are suitable feeds for HTL. Additional residues are removed at later stages in both procedures, which may also prove to be viable HTL feed. The quality and quantity of biocrude produced from these residues must be determined through experiments in order to deduce the viability of the combined uric acid extraction and HTL process. Furthermore, the feasibility of splitting the fresh chicken manure feed for HTL and uric acid extraction, respectively, should be investigated as it may prove to be the most profitable arrangement. Additionally, both processes show flexibility in the solvents used and thus various tests should also be performed with the aim of maximising profitability as well as sustainability. Overall, considering the high value of uric acid as well as the various extraction options available, this combined procedure could prove economically beneficial in aiding the industrial implementation of HTL and consequently the feasibility of the biorefinery in question.

3. Phosphate Analysis

Considering the current state of phosphate rock reserves as well as the global misuse of phosphorus, efficient phosphorus recovery techniques are vital in order to sustain food security while further reducing contamination-related problems. Research on the recycling of phosphorus from HTL products, when using livestock manures, has seen increasing attention and has shown great promise as an alternative source for valuable phosphorus-containing compounds [22]. The following section discusses the current knowledge on phosphorus behaviour during HTL as well as the prospects associated with its extraction.

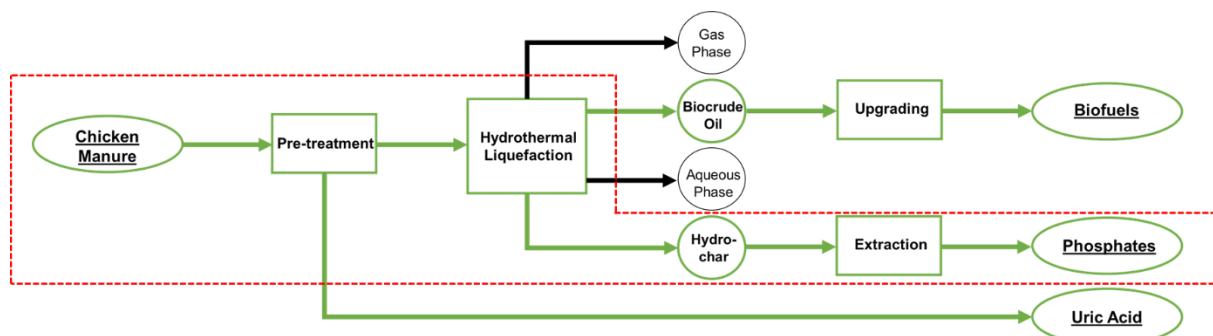


Figure 22: Showing the aspect of the biorefinery in focus for the phosphate analysis (indicated by red-dotted line)

Phosphorus Behaviour during HTL

It is largely accepted that during hydrothermal processing, the phosphorus-containing compounds in the feedstock are hydrolysed or dissolved into orthophosphates [25]. These orthophosphates either remain in the aqueous phase or are then complexed with inorganics, such as calcium, to form stable species that are precipitated or adsorbed to the hydrochar [25, 74]. The formation of orthophosphates is beneficial as they are the most desirable species for phosphorus reclamation, which suggests hydrothermal treatments enhance phosphorus recovery potential [25].

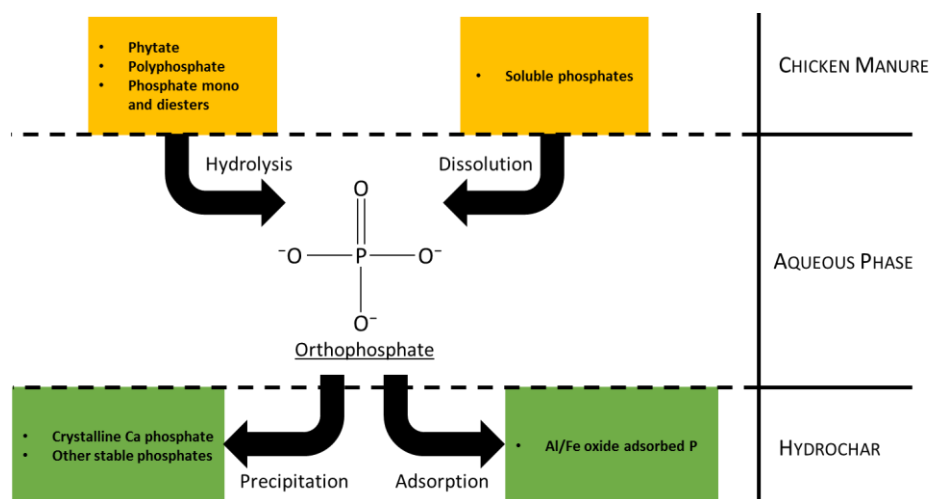


Figure 23: Schematic illustration of possible mechanisms of phosphorus transformation during HTL of chicken manure. Adapted from [25].

It has been determined that the amount of phosphorus present in the hydrochar is primarily affected by temperature, catalyst used, feedstock composition as well as the presence of inorganics such as Ca, Mg, Al and Fe [9, 22, 25, 36]. Hydrothermal carbonisation (HTC) experiments performed on chicken manure reported the following results: Heilmann et al. [36] found that 73-92% of the phosphorus is located in the hydrochar following HTC at 200-250°C and Huang et al. [74] achieved almost 100% recovery of phosphorus in the hydrochar after HTC at both 175 and 225°C [36]. Furthermore, studies have shown that the recovery of phosphorus in the hydrochar increases with an increase in temperature under hydrothermal conditions [22, 25, 32]. Since HTC is an almost identical thermochemical technique as HTL, only performed at lower temperatures, HTL is expected to have a similar or greater recovery of phosphorus in the hydrochar. Based on this, the hydrochar product is the most promising source for phosphorus reclamation following HTL of chicken manure.

The publication by Ekpo et al. [32] was the only HTL study found using chicken manure, where the aqueous and hydrochar products were quantitatively analysed for the presence of phosphorus. HTL was performed at operating conditions of 350°C, 18 MPa, 60 min retention time, 10 wt% solid content, with a heating rate of 10°C /min. These conditions gave the second highest biocrude yield out of the studies summarised in Table 3. It was found that approximately 7% of all phosphorus went to the aqueous phase, 50% went to the hydrochar and the rest is assumed to have either been undetected or migrated to the biocrude. The calculation for phosphorus recovery in the hydrochar can be seen in Appendix part 3. Migration to the hydrochar was lower than expected, which may be due to detection limitations associated with colorimetry; the analytical technique used. Irrespective of the accuracy, the study performed by Ekpo et al. [32] determined that the amount of phosphorus in the hydrochar was 6.44 g/kg of dry chicken manure fed. This is still significant, especially when considering the enormous quantities of chicken manure produced globally and the large complexes within which phosphorus exists. The calculation for this can be seen in Appendix part 4.

The form in which phosphorus (P) is present in the hydrochar has been found to be highly dependent on the inorganics present in the feedstock; especially calcium (Ca), copper (Cu), zinc (Zn), magnesium (Mg), aluminium (Al) and iron (Fe) [9, 25, 36]. This is because these multivalent metals form insoluble phosphate complexes during hydrothermal processing, which are the phosphorus species found in the hydrochar [32, 36].

Chicken manure contains high levels of metals, predominantly calcium and magnesium as seen in Table 1. It has been observed that most of the Ca, Mg, Al, Fe and P species present in chicken manure migrated to the hydrochar during HTL [13, 32]. The study performed by Ekpo et al. [32] found that the hydrochar contained 40230 mg/kg phosphorus, 61740 mg/kg calcium, 19040 mg/kg magnesium and only 2120 and 2090 mg/kg of iron and aluminium respectively. These were the dominant inorganic elements in the hydrochar. The metal to phosphorus ratios for potential phosphate salts are given in Table 6 below, which are based on the most prevalent phosphorus species determined in previous hydrothermal experiments [36]. Ekpo et al. [32] achieved a Ca:P of 1.53, Mg:P of 0.473, Fe:P of 0.053 and an Al:P of 0.052, for which the calculations can be seen in Appendix part 5. These results suggest that the phosphorus species present in the hydrochar were primarily in the form of calcium phosphates.

Table 6: Showing the metal to phosphorus ratios for potential phosphate salts present in the hydrochar [36]

Phosphate Salt	Metal to Phosphorus ratio (weight basis)
Tricalcium Phosphate ($\text{Ca}_3(\text{PO}_4)_2$)	1.93
Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$)	2.15
Magnesium Phosphate ($\text{Mg}_3(\text{PO}_4)_2$)	1.16
Iron Phosphate (FePO_4)	1.76
Aluminium Phosphate (AlPO_4)	0.87

This deduction is further supported by published literature. Experiments have confirmed that under hydrothermal conditions, phosphorus-containing compounds in chicken manure are predominantly converted to insoluble calcium phosphate species due to the abundance of calcium [9, 25, 36, 74]. Furthermore, the formation of calcium phosphate species under hydrothermal conditions is well established as it is pertinent to many geological processes [25, 74].

Phosphate Extraction

Phosphorus is conventionally extracted from solid biowastes by solubilising in an aqueous phase (anaerobic digestion or chemical extraction) followed by recovery through precipitation, adsorption or ion exchange [25]. Previous studies on HTC hydrochar derived from chicken manure have deduced that acid extraction followed by precipitation with a base is the most effective reclamation technique [25, 36].

Heilmann et al. [36] performed HTC on chicken manure and reported an 89% overall recovery of phosphorus following extraction from the hydrochar product. Extraction was achieved using excess hydrochloric acid (HCl), followed by addition of a base (sodium hydroxide) to achieve a pH of 9 after which the precipitate was filtered [36]. The phosphorus species extracted was determined to be predominantly in the form of tricalcium phosphate, which is a desirable component of diminishing phosphate rock [36]. Tricalcium phosphate is applicable for soil fertilisation due to its slow release rate and moreover will be an almost billion-dollar commodity by 2025 [22, 27, 28]. A study performed by Huang et al. [74] achieved a 91% recovery of phosphorus from the hydrochar following HTC of chicken manure at 225°C. This was also achieved using HCl extraction followed by basic precipitation. However, Huang et al. [74] deduced that the predominant calcium phosphate species present was hydroxyapatite (HA), which is further supported by Gupta [75] and Huang et al. [25]. In addition, Bircan et al. [99] found that 27.9% of the phosphorus in chicken manure was converted to HA, found in the hydrochar, following hydrothermal gasification at 400°C and 26-27 MPa. Hydroxyapatite (HA), like tricalcium phosphate, is also a desirable component of diminishing phosphate rock. It is used extensively in pharmaceutical and medical applications and is furthermore expected to be a 3 billion-dollar commodity by 2025 [23, 82]. Overall, regardless of which calcium phosphate species is most abundant, these results prove that HTL of chicken manure can potentially alleviate reliance's on diminishing phosphate rock reserves [9, 22, 23].

Tricalcium phosphate has a current selling price of approximately \$600-1000 per tonne whereas hydroxyapatite sells for at least \$9900 per tonne [83, 84]. The study by Ekpo et al. [32], mentioned previously, found that 6.44 kg of phosphorus was present in the hydrochar per tonne of chicken manure fed during HTL. This translates to approximately \$19.3-32.2 worth of tricalcium phosphate or \$344 worth of HA per tonne of chicken manure. This indicates that the presence of HA would prove significantly more advantageous economically. The calculation for this can be seen in Appendix part 6.

Moreover, the demand for calcium phosphates has significantly increased over the last few years due to increased food demand by the expanding population, continued excavation of diminishing phosphate rock reserves as well as the loss of phosphorus to the environment [24, 25, 85]. This suggests that the presence of tricalcium phosphate may also prove profitable in the future, which is well suited to the biorefinery in question because HTL is still an emerging technique [51].

Summary, Recommendations and Conclusions

Overall, despite the high phosphorus reclamation yields mentioned, none of the studies above quantified the purity or quantity of the calcium phosphate species extracted. This, along with the conflicting results pertaining to the exact phosphorus species present, indicates that further experimentation is needed. Thorough speciation is required in order to determine the type, purity and quantity of the phosphorus species present after extraction from the hydrochar. Multiple analytical techniques should be used such as ³¹P solid-state NMR spectroscopy, P X-ray absorption spectroscopy, ICP-MS and X-ray diffraction in order to attain conclusive

results [25, 36]. This speciation will allow for an accurate assessment on the feasibility of extracting the calcium phosphate species present.

In conclusion, during hydrothermal processing of chicken manure, phosphorus is predominantly converted to calcium phosphate species which are found in the hydrochar. These species are notably desirable constituents of diminishing phosphate rock reserves, which are the major source of the world's phosphorus [23]. Furthermore, these species have been proven to be readily extractable by acid treatment followed by basic precipitation, with recoveries of over 90% attained from hydrochar. Considering the limited phosphate rock reserves remaining as well as the four-fold increase in demand for phosphates over the last half-century, the reclamation of calcium phosphates from HTL hydrochar should be investigated further [24, 25, 85]. This reclamation could prove significantly advantageous in terms of future phosphorus security and may furthermore prove to be profitable, thus aiding the industrial implementation of HTL and the overall feasibility of the biorefinery in question.

Final Summary

Based on the biocrude, uric acid and phosphate analyses completed, the benefits and limitations associated with the biorefinery in question are summarised in Table 7 below:

Table 7: Showing a summary of the benefits and limitations associated with the novel biorefinery

Chicken Manure	Benefits	Limitations
Hydrothermal Liquefaction	<ul style="list-style-type: none"> - Produces energy rich fuels - Stabilises heavy metals - Kills pathogens - Destroys antibiotic resistant genes - Removes odorous compounds - Useful applications for by-products - Feed drying not required - > 75% reduction CO₂ emissions w.r.t fossil fuels - Feasible w.r.t other biofuel technologies - In combination with upgrading can produce functional biofuels - Significant optimisations can still be made 	<ul style="list-style-type: none"> - Unfeasible w.r.t fossil fuels - Has not reached commercial status - Harsh operating conditions - Limited literature on chicken manure - Varying feed compositions - Limited knowledge on reaction mechanisms - High nitrogen content in biocrude
Uric Acid Extraction	<ul style="list-style-type: none"> - Readily extractable - High value - Abundant in chicken manure - May improve overall biorefinery feasibility - Various integration options 	<ul style="list-style-type: none"> - Compatibility with HTL unknown - Competing microbial degradation of uric acid - Feasibility unknown
Phosphate Extraction	<ul style="list-style-type: none"> - Readily extractable - Desirable compounds present - May improve overall biorefinery feasibility - Alleviates reliance's on diminishing reserves - Help ensure future food security 	<ul style="list-style-type: none"> - Uncertainties in dominant species present - Purity of extracted species is unreported - Feasibility unknown

Note: w.r.t – with respect to.

Conclusions

The biocrude analysis showed that chicken manure can be effectively used as a feedstock for HTL to produce an energy-rich fuel, with yields of greater than 17 wt% (dry basis) achieved on a lab scale via batch processing. Studies produced biocrude products with HHV values up to 37.0 MJ/kg, which shows a significant improvement from the values deduced for the respective feedstocks (10.7-18.1 MJ/kg). The properties of the biocrude obtained do not comply with common fuel standards, however the successful upgrading of swine manure biocrude to biodiesel demonstrates that upgrading chicken manure biocrude is possible, but moreover, the high nitrogen content may require additional treatment. Furthermore, the costs associated with HTL and upgrading of various feedstocks have proven to be economically uncompetitive with fossil fuels but economically competitive with other biofuel technologies, which shows promise for its future implementation. Moreover, it has been proven that HTL when using chicken manure significantly stabilises heavy metals, destroys antibiotic resistance genes, kills pathogens, removes odorous compounds and has possible applications for all the by-products produced. Overall, the results analysed prove that HTL of chicken manure, in combination with upgrading, has great potential in producing functional biofuels while eliminating several disposal-related problems.

The uric acid analysis conducted resulted in the conclusion that UA must be extracted prior to HTL, due to decomposition that occurs under HTL conditions. Based on the two procedures assessed, uric acid can be effectively extracted from chicken manure with yields above 80% and purities of up to 99.9%. Furthermore, both procedures produce large quantities of feed and supplement valued residues which suggests they are compatible with HTL to produce biocrude. Additionally, residues are removed at later stages in both processes which may also prove to be viable HTL feed. However, the compatibility of these residues with HTL needs to be tested further, taking into consideration the amount of uric acid extracted, the biocrude quantity and quality obtained and as such the overall feasibility of this combined method. Lastly, the feasibility of splitting the fresh chicken manure feed for HTL and uric acid extraction, respectively, should be investigated as it may prove to be the most profitable arrangement. Overall, considering the high value of uric acid as well as the various extraction options available, this combined procedure could prove profitable and thus aid the feasibility of the biorefinery in question.

The phosphate analysis established that during HTL of chicken manure, phosphorus is predominantly converted to calcium phosphate species which are found in the hydrochar. These species are notably desirable constituents of diminishing phosphate rock reserves. Furthermore, these species have been proven to be readily extractable through acid dissolution followed by basic precipitation, with HTC experiments demonstrating that more than 90% of the phosphorus from the hydrochar could be recovered. However, the type, purity and quantity of the calcium phosphate species extracted following HTL of chicken manure remains largely uncertain. Regardless, this reclamation could prove significantly advantageous in terms of future phosphorus security and may furthermore prove to be profitable, especially if hydroxyapatite is predominant, thus aiding the overall feasibility of the biorefinery in question.

Ultimately, considering the potential economic benefits of combined uric acid and phosphate extraction with HTL, along with erratic petroleum prices, new developments in HTL operations as well as potential government support; the biorefinery in question could prove feasible in the near future. However, due to the limited scope of this analysis, it is imperative that laboratory testing is performed in order to reach definitive conclusions. It is recommended that the optimal HTL and upgrading conditions for processing chicken manure be investigated. This will allow

for a more accurate conclusion as to the feasibility and competitiveness of the final biofuel product. Furthermore, tests should be conducted on the residues produced during uric acid extraction to determine their compatibility with HTL and additionally thorough speciation of calcium phosphates following HTL should be performed in order to deduce the feasibility of their extraction. Lastly, it is recommended that the extraction of other chemicals formed during HTL of chicken manure be investigated. This would maximise the potential of chicken manure treatment with HTL and consequently promote its competitiveness on a commercial scale.

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Appendix

1. From [34]

HTL of poultry manure in combination with HTL produces 494.50 kg CO₂-eq/tonne of feedstock

Biocrude yield: 47.11 wt% therefore 0.4711 tonnes of biocrude/tonne of feedstock

Biocrude HHV: 40 MJ/kg (a safe estimation was made)

1 MJ = 0.2778 kWh

Therefore:

$$\frac{494.50 \text{ kg CO}_2 - \text{eq}}{1 \text{ tonne feedstock}} \times \frac{1 \text{ tonne feedstock}}{0.4711 \text{ tonnes biocrude}} \times \frac{1 \text{ tonne biocrude}}{1000 \text{ kg biocrude}} \times \frac{1 \text{ kg biocrude}}{40 \text{ MJ}} \times \frac{1 \text{ MJ}}{0.2778 \text{ kWh}} \times \frac{1000 \text{ g CO}_2 - \text{eq}}{1 \text{ kg CO}_2 - \text{eq}} = \mathbf{94.5 \text{ g CO}_2 - \text{eq/kWh}}$$

2. From [31, 68, 71]

Uric acid content ranges from 15-57 kg/tonne of chicken manure (CM)

Uric acid selling price: \$12000/tonne

Therefore:

$$\frac{15 \text{ kg UA}}{1 \text{ tonne CM}} \times \frac{1 \text{ tonne UA}}{1000 \text{ kg UA}} \times \frac{\$12000}{1 \text{ tonne UA}} = \mathbf{\$180 \text{ UA per tonne CM}}$$

$$\frac{57 \text{ kg UA}}{1 \text{ tonne CM}} \times \frac{1 \text{ tonne UA}}{1000 \text{ kg UA}} \times \frac{\$12000}{1 \text{ tonne UA}} = \mathbf{\$684 \text{ UA per tonne CM}}$$

3. From [32]. (Phosphorus – P) *recovery of phosphorus in aqueous phase given in paper

Chicken manure (CM) feed on a dry basis: 12870 mg P/kg CM

Hydrochar: 40230 mg P/kg hydrochar

[32] achieved a 16.0 wt% yield of hydrochar on a dry basis.

Assume: 1 kg dry CM feed. This gives 0.160 kg hydrochar.

$$1 \text{ kg dry CM} \times \frac{12879 \text{ mg P}}{\text{kg dry CM}} \times \frac{1 \text{ g P}}{1000 \text{ mg P}} = \mathbf{12.9 \text{ g P in dry CM}}$$

$$0.160 \text{ kg hydrochar} \times \frac{40230 \text{ mg P}}{\text{kg hydrochar}} \times \frac{1 \text{ g P}}{1000 \text{ mg P}} = \mathbf{6.44 \text{ g P in hydrochar}}$$

Therefore, P yield in hydrochar = $\frac{6.44}{12.9} \times 100\% = 49.9\%$

4. From [32] (Phosphorus – P)

Chicken manure (CM) feed on a dry basis: 12870 mg P/kg CM

Hydrochar: 40230 mg P/kg hydrochar

[32] achieved a 16.0 wt% yield of hydrochar on a dry basis.

Therefore:

Assume: 1 kg dry CM -> 0.160 kg of hydrochar

$$\frac{0.160 \text{ kg hydrochar}}{\text{kg dry CM}} \times \frac{40230 \text{ mg P}}{\text{kg hydrochar}} \times \frac{1 \text{ g P}}{1000 \text{ mg P}} = 6.44 \text{ g P in hydrochar per kg dry CM fed}$$

5. From [32]

Main inorganics in hydrochar:

40230 mg/kg phosphorus (P), 61740 mg/kg calcium (Ca), 19040 mg/kg magnesium (Mg), 2120 iron (Fe) and 2090 mg/kg aluminium (Al).

Therefore:

$$\text{Ca:P} = \frac{61740}{40230} = 1.53$$

$$\text{Mg:P} = \frac{19040}{40230} = 0.473$$

$$\text{Fe:P} = \frac{2120}{40230} = 0.0527$$

$$\text{Al:P} = \frac{2090}{40230} = 0.0520$$

6. From [32] -> 6.44 kg of P was present in the hydrochar per tonne of chicken manure fed

Molar masses: Ca – 40.1 g/mol, P – 31 g/mol, O – 16 g/mol, H – 1 g/mol

Tricalcium Phosphate (TCP) (Ca₃(PO₄)₂):

Molar mass Ca₃(PO₄)₂ = (3×40.1) + (2×31) + (8×16) = 310.3 g/mol

Assume: 1 mol of Ca₃(PO₄)₂ (which converts to 2 mol of P)

1 mol Ca₃(PO₄)₂: 1 mol x 310.3 g/mol = 310.3 g of Ca₃(PO₄)₂

2 mol P: 2 mol x 31 g/mol = 62 g of P within 1 mol of TCP

$$\frac{310.3 \text{ g TCP}}{62 \text{ g P}} = 5.00$$

Therefore 6.44 kg of P in the hydrochar per tonne of chicken manure (CM) fed converts to:

$$\frac{6.44 \text{ kg P hydrochar}}{1 \text{ tonne of CM fed}} \times \frac{5 \text{ kg of TCP}}{1 \text{ kg P}} = 32.2 \text{ kg TCP in hydrochar per tonne CM fed}$$

Tricalcium phosphate has a current selling price of \$600-1000 per tonne.

Therefore:

$$\frac{32.2 \text{ kg TCP}}{1 \text{ tonne CM fed}} \times \frac{1 \text{ tonne TCP}}{1000 \text{ kg TCP}} \times \frac{\$600}{1 \text{ tonne TCP}} = \mathbf{\$19.3 \text{ TCP per tonne CM fed}}$$

$$\frac{32.2 \text{ kg TCP}}{1 \text{ tonne CM fed}} \times \frac{1 \text{ tonne TCP}}{1000 \text{ kg TCP}} \times \frac{\$1000}{1 \text{ tonne TCP}} = \mathbf{\$32.2 \text{ TCP per tonne CM fed}}$$

Hydroxyapatite (HA) (Ca₁₀(PO₄)₆(OH)₂)

Molar mass Ca₁₀(PO₄)₆(OH)₂ = (10×40.1) + (6×31) + (26×16) + (2×1) = 1005 g/mol

Assume: 1 mol of Ca₁₀(PO₄)₆(OH)₂ (which converts to 6 mol of P)

1 mol Ca₁₀(PO₄)₆(OH)₂ : 1 mol x 1005 g/mol = 1005 g HA

6 mol P: 6 mol x 31 g/mol = 186 g P within 1 mol of HA

$$\frac{1005 \text{ g HA}}{186 \text{ g P}} = 5.40$$

Therefore 6.44 kg of P in the hydrochar per tonne of chicken manure (CM) fed converts to:

$$\frac{6.44 \text{ kg P hydrochar}}{1 \text{ tonne of CM fed}} \times \frac{5.4 \text{ kg of HA}}{1 \text{ kg P}} = 34.8 \text{ kg TCP in hydrochar per tonne CM fed}$$

Hydroxyapatite has a current selling price of at least \$9900 per tonne.

Therefore:

$$\frac{34.8 \text{ kg HA}}{\text{tonne CM fed}} \times \frac{1 \text{ tonne HA}}{1000 \text{ kg HA}} \times \frac{\$9900}{1 \text{ tonne HA}} = \mathbf{\$344 \text{ HA per tonne CM fed}}$$