

HYDROTHERMAL VALORIZATION OF AGRICULTURAL
WASTE- BIOCRUDE OIL UPGRADING AND NUTRIENT
RECOVERY

A Dissertation

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ABSTRACT

With sustainability issues increasing in importance, there is always a growing need for proper food/agricultural waste management. With our increasing global population, the need is only intensified. Currently, a major fraction of the food waste is directed toward landfill disposal without recovering any energy or other marketable by-products. This practice leads to significant methane emissions impacting climate change. Other commercial food waste management methodologies involve incineration and anaerobic digestion, while they address energy recovery from waste, there remains a key question of how best to deal with wet waste streams. Incineration including drying which is very energy intensive and anaerobic digestion results in incomplete conversion of the organic carbon to biogas with a large amount of wet residual digestate. As a result, both methods are not optimal for treating dilute wet wastes.

Hydrothermal treatment provides an attractive alternative to more effectively valorize wet agricultural/food wastes to produce energy-rich (bio-crude oil) and nutrient-rich (aqueous phase) products that can be reapplied back to the industry creating a circular bioeconomy. Hydrothermal valorization of manures, food wastes, sewage sludge, etc. have been demonstrated in the literature, but these biomass feedstocks are more nitrogenous and oxygenated in nature subsequently resulting in bio-oils with a lower heating value compared to petroleum-based crude oil. This study makes use of a Two-Stage hydrothermal treatment process to effectively valorize chicken manure and partition nitrogen into the aqueous phase (nutrient-rich) and produce an upgraded

biocrude-oil (energy-rich) with a better heating value for direct application as a drop-in fuel. A mechanistic study was performed to understand the underlying degradation mechanisms involved in the wet biomass conversion that resulted in bio-oil upgradation with changing experimental parameters including temperature, reaction time, and pH. The novelty lies in the addition of a homogeneous reusable acid catalyst (acetic acid) in studying the improvement in bio-oil yields and HHV.

BIOGRAPHICAL SKETCH

Dharani Prasad Vadlamudi was born on 19th February 1999 to Sri Krishna Vadlamudi and Suvarna Phani Movva in Gudivada, Andhra Pradesh, India. He grew up with most of his schooling done in Hyderabad, India where he also grew fond of chemistry and mathematics which ultimately led him to pursue a chemical engineering bachelor's degree at the Indian Institute of Petroleum and Energy (IPE), Visakhapatnam, India. After his graduation in 2020 from IPE, he gained professional experience in the Oil & Gas sector by working for almost a year as an engineering officer in the operations department at the downstream oil refinery. While he gained industry experience, he felt the need to pursue further studies by pursuing a graduate degree program. What inspired him was to pursue in sustainability space but still make use of his experience in the energy sector, this led him to start a Master of Science graduate program at Cornell in 2021 under the supervision of Dr. Jefferson W. Tester and Dr. Xingen Lei on biofuels research work presented in this thesis.

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CHAPTER 1

INTRODUCTION

Livestock and manure as the largest source contribute about 1/3 of the total methane emissions, whereas landfill accounts for 1/10 of the global methane emissions (World GHG Emissions in 2016, Climate Watch, World Resource Institute 2020)Click or tap here to enter text.. A major challenge in both developed and developing countries is to manage waste in terms of collecting, recycling, and treatment of wastewater and solid waste. Importantly, public health and environmental benefits are linked to effective waste management and improved the quality of life metrics. The reduction in GHG emissions should relate to integrated waste management. Solid waste has the potential for significant energy resources through waste management technologies that are mature and have been deployed for many years (incineration, anaerobic digestion, etc.). There are often different mitigation strategies including a range of technologies where no single option is not always the best choice rather multiple measures where collective implementation can reduce GHG emissions.

1.1. Global Waste Management

Solid waste and wastewater generation data varies regionally and also the lack of data can be a major problem for many countries when assessing GHG emissions. Solid waste generation varies from less than 0.1 t/capita/year in low-income countries to 0.8 t/capita/year in high-income countries (Bogner, J., 2007). A major distinction is how waste generation is linked to population and wealth- richer communities are generalized by higher rates of waste generation per capita compared to less-income societies. Table 1 mentioned below shows the municipal generation rates with relative income levels to give a comparison of the role income plays towards waste.

Table 1 Municipal solid waste generation relative to income levels (Bogner, J., 2007.)

Country	Low Income	Middle Income	High Income
Annual income (US\$/cap/ yr)	825-3,255	3,256-10,065	>10,066
Municipal solid waste generation rate (t/cap/ yr)	0.1-0.6	0.2-0.5	0.3 to >0.8

The total municipal solid waste produced in the U.S. in 2018 was 292.4 million tons and only 69 million tons were recycled, and 25 million tons were composted, this accounts for 32.1% of the solid waste (EPA 2006). Fig. 1 shows how the different waste management strategies are used for the municipal solid waste generated in the U.S.

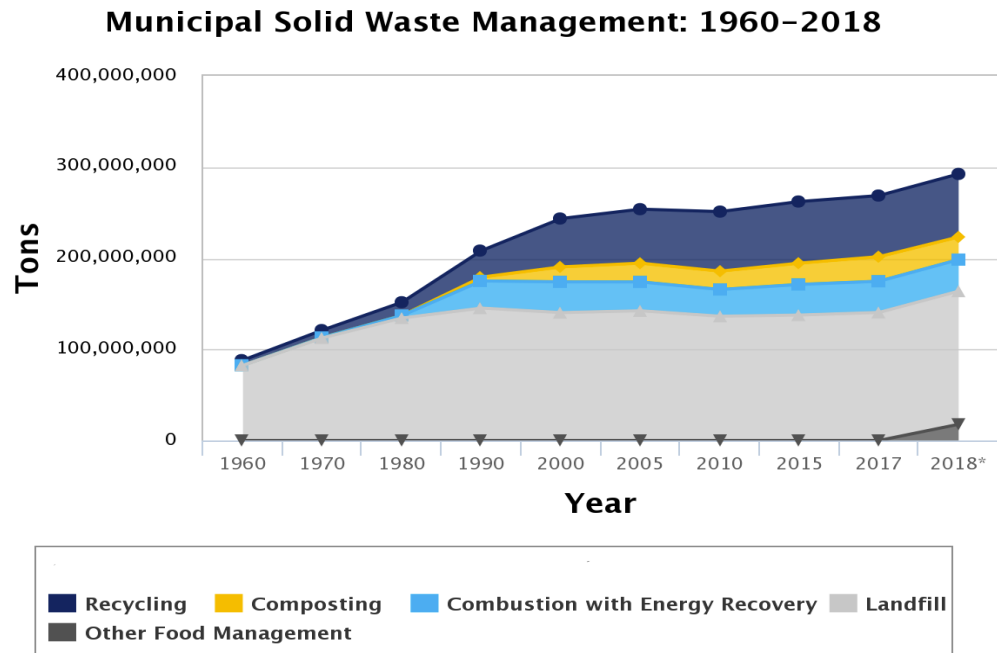


Figure 1 U.S Changes in Municipal Solid Waste Management (EPA 2018)

From the figure, it is evident that more than half of the solid waste goes to landfill. This can contribute to significant GHG emissions. In terms of materials composition from solid waste, paper and food constitute a major portion as shown in Fig. 2. Most of the

paper and paperboard gets recycled, which leaves the management of food waste as an important proportion in solid waste generation.

Total MSW Generated by Material, 2018

292.4 million tons

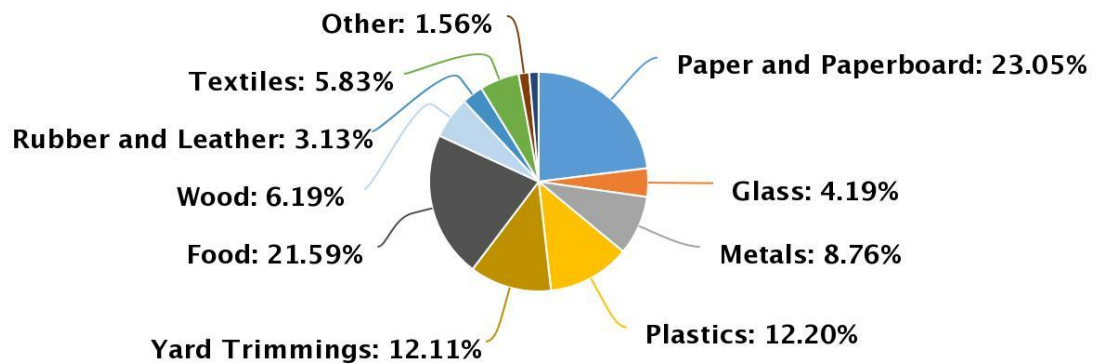


Figure 2 U.S. Municipal Solid Waste (MSW) Generation by Material (EPA 2018)

1.2. Commercial Food Waste Treatment

Food waste from Municipal Solid Waste in the U.S. in 2018 was 63.1 million tons. More than half of food waste goes to landfill as shown in Fig. 3.

Food Waste Management, 2018

63.1 million tons

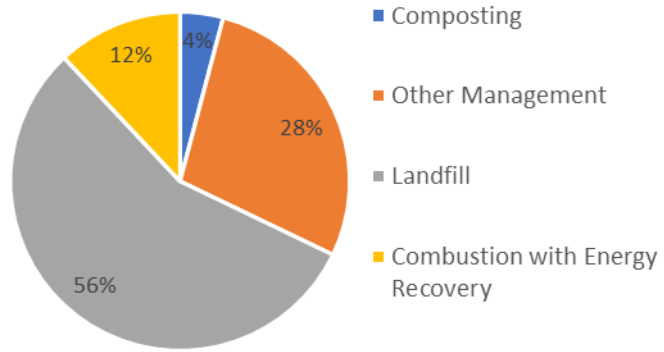
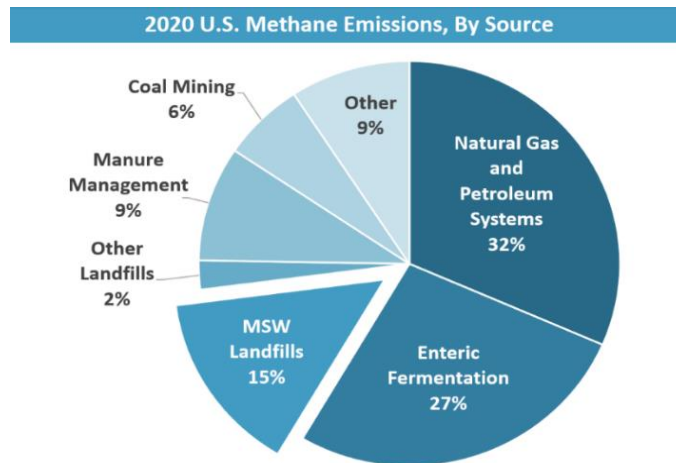


Figure 3 Food Waste Management from MSW in the U.S. (EPA 2018)

Directing food waste to landfill will lead to significant methane emissions. In 2020, Municipal Solid Waste (MSW) is the third largest source of methane emissions in the United States (EPA 2020) as shown in Fig. 4.



Note: All emission estimates from the Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2020. U.S. EPA. 2022.

Figure 4 United States Methane Emissions from various sources in 2020 (EPA 2020)

Organic/Food waste from MSW is the major contributor to methane emissions. Other Food Management strategies contributing 28% of Food-Waste in Fig. 3 denote co-digestion/anaerobic digestion, bio-based products, land application, and diverting towards wastewater treatment. Food Waste managed through combustion for energy recovery accounts for 12% where the incineration process occurs at mass burn facilities. The incineration process can be energy intensive at high temperatures for complete combustion in the presence of excess air. Current non-renewable thermal energy inputs give a carbon footprint to such a system.

1.2.1. Landfill

As mentioned before, more than 50% of food waste is sent to landfills. Depending on the local jurisdictions, the percentage of food waste in Municipal Solid Waste (MSW) varies from 25-65% (Banks, C.; 2018). As shown in Fig. 2, Food Waste comprises 21.59% in the U.S. in 2018. Even in Canada, most of the food waste is directed to landfills, Animal Feed, and some for composting or Anaerobic Digestion (Gooch, M., 2019). Food Waste can contain lignin and lignocellulosic materials that can be hard to convert in anaerobic digestion thus leading to less biomethane potential (Kibler et al., 2018). But direct disposal to landfill is not the solution when dealing with heterogeneous mixtures, proper pretreatment, and sorting are important to valorize the waste streams. Avoiding Landfill becomes prominent in GHG emission reduction due to methane emissions from landfills having a Global Warming Potential (GWP) of 27-30 over 100 years (EPA's U.S. GHG emissions and sinks inventory).

1.2.2. Anaerobic Digestion (AD)

Anaerobic Digestion is a process that leads to the breakdown of organic matter by bacteria (methanogens) in the absence of oxygen-producing methane and carbon dioxide (biogas). Biogas is further upgraded to separate CH₄ from CO₂ and the biomethane separated can be used for various energy demands. The side product of AD is a digestate that contains a significant amount of unconverted biomass and can be utilized for soil amendment, animal bedding, or other agricultural applications. Fig. 5 represents the different feedstocks for AD along with applications of the products.

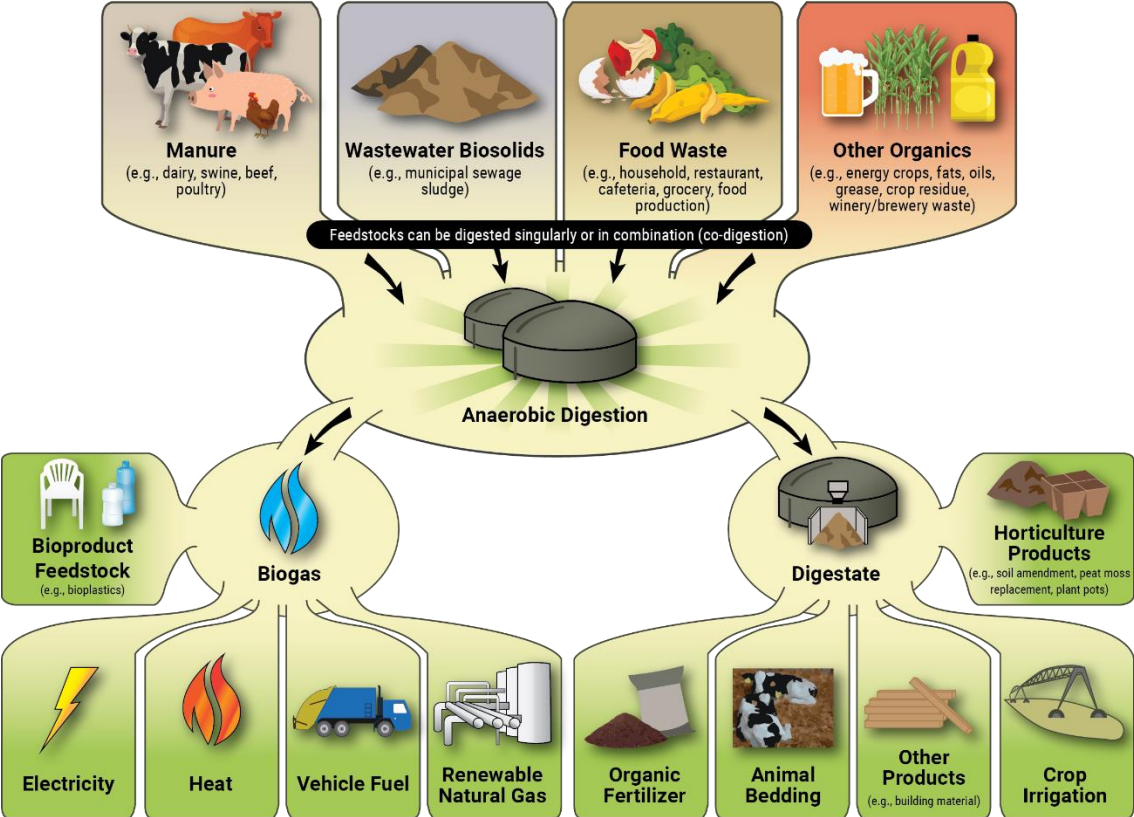


Figure 5 Flow of Feedstocks to AD with conventional products utilization (EPA, 2023)

1.2.3. Incineration

Incineration involves the direct burning of MSW at high temperatures in the presence of excess air. It can become more energy intensive when dealing with wet waste, but the energy generated is used for power generation in commercial plants thereby reducing the waste to landfills ('The Research on Food Waste Pre-Treatment Technology for Incineration in Malaysia', 2020). Currently, there are 75 facilities in the United States for recovering energy from waste through combustion. A typical waste-to-energy (WTE) plant generates 550 kWh per ton of waste (Kaplan et al., 2009). This can be seen as a better alternative compared to landfill. From Fig. 2, only 12% of food waste is directed to combustion for energy recovery accounting for only a small portion of the U.S. waste management system. Generally, regions that are denser and land limited tend to have greater incineration facilities compared to the U.S. where land limitation is not a problem. Another important factor to be considered is the fly ash that is produced from such facilities after combustion, proper collection and regulation of less-dense fly ash are important to ultimately divert the ash residue to landfill.

1.2.4. Composting

Composting takes place in a controlled environment in the presence of oxygen (aerobic conditions) through natural decomposition where the product formed can be used as a soil amendment. Quite often composting can result in methane emissions due to inadequate access to oxygen during decomposition. Composting can also be done right at the household in a backyard by using a mixture of carbon-rich ("browns") like dry leaves, plant stalks, and twigs and nitrogen-rich materials ("greens") including food scraps. Only 6% of total food waste is currently composted in the U.S. as shown in Fig. 2, which can be further increased through in-house treatments.

Apart from the commercial food waste management techniques mentioned above, there are many ways to valorize food waste to make useful products for application to different sectors. Fig. 6 depicts the different valorization pathways for food waste where different pretreatment and stages are described based on the feedstock (Roy et al., 2023). Usually, Food Waste has a higher moisture content which can make hydrothermal treatment processes like hydrolysis, carbonization, and liquefaction suitable. Such treatments will be the focus of this study to deal with wet waste like cattle and other animal manure or other wastes with high moisture content including food waste.

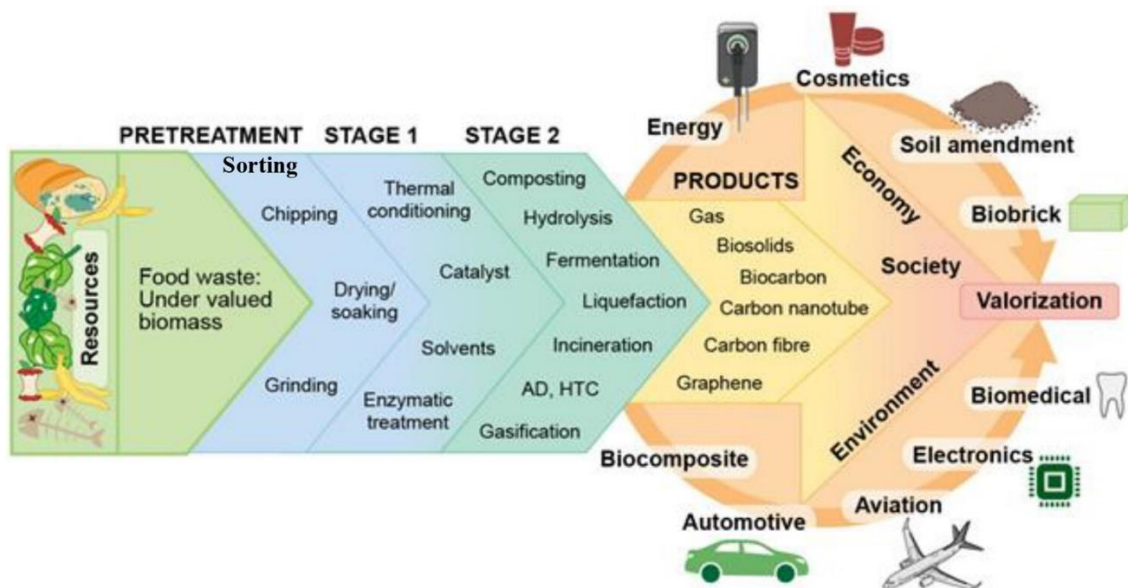


Figure 6 Food Valorization Processes (Roy et al., 2023)

CHAPTER 2

MOTIVATION & APPROACH FROM LITERATURE

2.1. Previous Studies

2.1.1. Biomass Feedstocks

Biomass feedstocks including food waste, manure, sewage sludge, digestate, etc. contain significant amounts of nitrogen and oxygen (Cabrera et al., 2022; Pecchi et al., 2022; Posmanik et al., 2018; Sudibyo & Tester, 2023). Table 2 shows different feedstock elemental compositions depicting O and N content. The table also provides estimates of the higher heating value (HHV) using Dulong-Berthelot empirical equation (Motavaf et al., 2021).

$$HHV \left(\frac{MJ}{kg} \right) = 0.3414C + 1.4445 \left(H - \frac{N + O - 1}{8} \right) + 0.093S$$

In this study, sulphur is not accounted for since it does not affect the HHV due to its low range of 0.2-1 wt% (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Q. Li et al., 2021; Motavaf et al., 2022).

Table 2 Elemental Composition of Different Biomass Feedstocks (wt%)-this study involves chicken manure (Cabrera et al., 2022; Pecchi et al., 2022; Posmanik et al., 2018; Sudibyo & Tester, 2023)

Feedstock	Digestate	Cow Manure	Digestate Manure	Food Waste	This Study
C	30.3	34.3	34	53.9	36.5
H	5.4	3.7	4.7	8.9	5
N	4.8	2.3	3.2	1.7	4.3
O	23.7	25.9	43.4	33.7	24.5
HHV (MJ/kg)	13.7	13.3	10.4	26	14.7

Such high O and N content can be transferred to biocrude oils leading to undesirable properties like reduced HHVs. Such characteristics of the oil will also lead to poisoning of the catalyst when upgradation of the oil is required to reach transportation fuel quality (Montero-Hidalgo et al., 2019). Understanding the migration of N and O is thus important to optimize the operating conditions and maximum partition of such elements into the aqueous phase. Nitrogen retained in the bio-crude oil is also not good as a fuel since it leads to NO_x emissions upon combustion (Galadima & Muraza, 2018).

In order to reduce N-content in biocrude oils, one can look at a two-stage process where N is partitioned into the aqueous phase in the first stage and the hydrochar is used as a feedstock for high-temperature liquefaction in the second stage. Knowledge of using and optimizing different process conditions including temperature, reaction time, and pH become important that are governing the reaction mechanism and ultimately the fate of oil yield and quality (N and O content) (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Gupta et al., 2020; L. Li et al., 2013; J. Lu, Li, et al., 2018; Saqib et al., 2019; Tradler et al., 2018).

2.1.2 Hydrothermal Carbonization (HTC) and Hydrothermal Liquefaction (HTL)

Thermochemical processes like Hydrothermal Carbonization (HTC) and Hydrothermal Liquefaction (HTL) are promising thermochemical treatments for valorizing wet wastes into energy and nutrient-rich products (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Gupta et al., 2020; L. Li et al., 2013; J. Lu, Li, et al., 2018; Saqib et al., 2019; Tradler et al., 2018). HTC generally forms a carbonaceous solid product when the feedstock is treated at temperatures ranging from 160°C to 250°C apart from an aqueous phase solution and gas phase mostly comprising of CO₂ (Libra et al., 2011). The

carbonized solid produced has different applications ranging from a soil amendment (Zhang et al., 2019), to an adsorbent (Zhang et al., 2019), to a solid fuel (Akarsu et al., 2019; Bhakta Sharma et al., 2021; Sharma & Dubey, 2020). Understanding the migration of N and O into the aqueous phase in HTC is important when designing a two-stage process. There is little known about the effectiveness for HTC of treating chicken manure. For example, having a better understanding of the elemental distribution of %C and %N in the product phases would help optimize the process conditions for producing hydrochar. There are some limited studies looking at such process variables evaluate the factors that govern the migration of N during HTC for food waste (Motavaf et al., 2021) and swine manure (Yuan et al., 2018). Several other studies also show the HTC of chicken manure focusing on solid fuel properties with a limited aim of quantifying the N distribution in the phases (Hejna et al., 2022; Q. Li et al., 2021; Zhou et al., 2019). Unfortunately, this earlier work failed to provide sufficient quantitative understanding of reaction times and selectivities. This study aims to evaluate different temperatures with different batch reaction times (30min and 60min) to quantify the yields of all three phases from the HTC of chicken manure as well as to track C and N recovery in the different phases.

Hydrothermal Liquefaction (HTL) is also a thermochemical process with temperatures ranging between 250 and 350°C and at pressures above the vapor pressure for water to maintain a the liquid phase at subcritical conditions (Cabrera & Labatut, 2021). With HTL process conditions, water behaves with unique properties where the ionic product (K_w) increases with increase in temperature. These properties facilitate the tunability of acid-base catalyzed reactions in subcritical water (Kumar, 2014) that distribute carbon containing compounds into energy-rich biocrude oil, an aqueous phase, solid

(hydrochar), and gaseous phase comprised mainly of CO₂. Such acid-base reactions follow fast hydrolysis, dehydration, and condensation of sugars, lipids, and proteins in subcritical conditions (Peterson et al., 2008). HTL reaction pathways and rates depend on the process parameters and feedstock characteristics, including temperature, reaction time, and pH. Hence, achieving high energy recovery in bio-oil and nutrient recovery in the co-products depends on the thermochemical changes occurring during these conversions to different products which in turn depends on the operating conditions and feedstock. Previous studies have shown different methods for optimizing HTL for different feedstocks (Ekpo, Ross, Camargo-Valero, & Fletcher, 2016; Ghanim et al., 2018; Song et al., 2017). Also, it is reported that for HTL, 280-320°C and 15-60 min as the ideal conditions for temperature and reaction time to produce higher yields of oil (Posmanik et al., 2017; J. Yang et al., 2019). The reaction time in this study for HTL treatments is set to 30 min since this was reported as the optimum condition for obtaining maximum biocrude yield from manures (J. Lu, Watson, et al., 2018; Yin et al., 2010).

2.2. Focus

2.2.1. Two-Stage Hydrothermal Treatment

Conventional single-step HTL is not an ideal path to produce low-N biocrude with high recovery of N in the co-product stream. Earlier studies have shown how HTC as a low-temperature process can be used as a pretreatment before performing liquefaction (J. Lu, Watson, et al., 2018; Motavaf et al., 2021). Furthermore two-stage hydrothermal processes are also introduced in previous studies, particularly for microalgae feedstock (Chakraborty et al., 2012; S. Wang et al., 2021). Often, the first stage is conducted at

low temperatures of about 160°C and the second stage at higher temperatures of 300°C or more to produce bio-oil with a reduced nitrogen content. While the two-stage concept is showing promise in improving the quality of the biocrude-oil, it can be coupled with a reduction in the quantity of the bio-crude generated w.r.t the feedstock (Du et al., 2012; Miao et al., 2012). Thus, it becomes important to understand the process conditions that optimize for both the quality and quantity of the biocrude-oil which include temperature, reaction time and the role of pH for both HTC and HTL processes.

This study will for the first time examine the effectiveness of a two-stage process with chicken manure as feedstock. There have also been several HTC and HTL studies of chicken/poultry manure (Ekpo, Ross, Camargo-Valero, & Williams, 2016; J. Lu, Li, et al., 2018; Matsumura et al., 2021). The research conducted here uses a two stage process to optimize yields of %C and %N recovery and to track the elemental distribution of products and develop plausible reaction mechanisms consistent with measured results. HTL was selected as a reference base case, performed in temperatures ranging from 250 to 350°C with a 30 min reaction time. Figure 7 shows the base case framework which involves direct hydrothermal liquefaction (HTL) of chicken manure and uses that to compare with results for the two-stage process. And as depicted in the schematic for the two-stage process there is HTC as a pretreatment step before HTL. For HTC, the temperatures in this study ranged from 160 to 250°C with reaction times of 30 and 60min to look at broader operating conditions compared to the literature focusing on specific temperatures and/or reaction time for chicken manure feedstock (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Hejna et al., 2022; Kantarli et al., 2016; Zhou et al., 2019). The solid product from the first stage after choosing the best-

optimized parameters is fed for liquefaction to produce bio-crude oil with lower N-content.

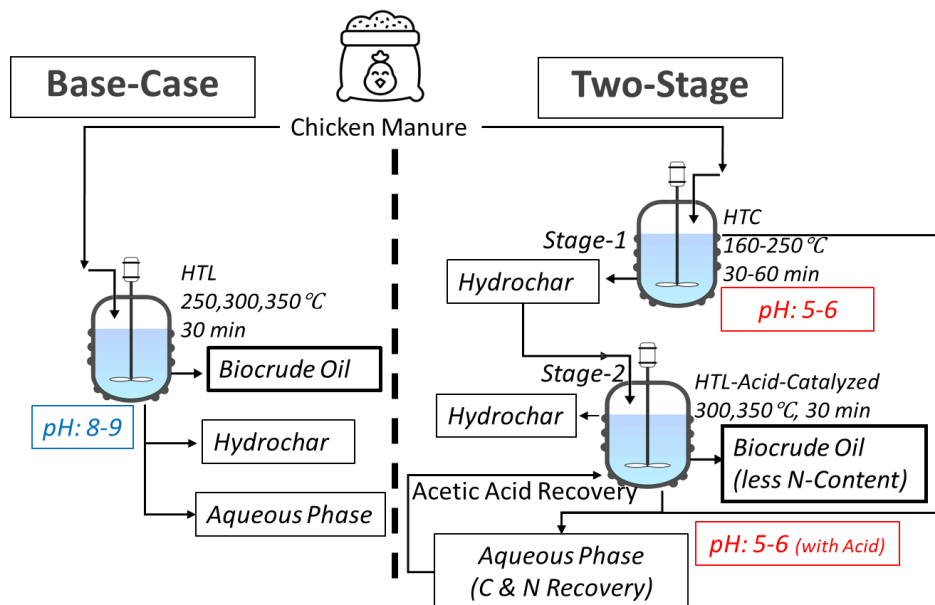


Figure 7 Two Pathways on Hydrothermal Treatment of Chicken Manure

2.2.2. Acid-Catalyzed Hydrothermal Liquefaction

Hydrothermal Liquefaction at high temperatures above 250°C occurs with water in a less polar state than at ambient conditions where the ionic product (K_w) increases promoting both acid and base-catalyzed ionic reactions. (Peterson et al., 2008). For example, under acidic conditions glucose degradation shifts toward producing 5-hydroxymethyl-furfural (HMF)(Yin & Tan, 2012) that can positively affect the HTL process and biocrude oil yield (Jin & Enomoto, 2011). Various homogeneous and heterogeneous catalysts have been used to affect the pH of the reaction which becomes crucial for biomass conversion. Many such homogeneous catalysts include acetic acid, formic acid, sulphury acid, phosphoric acid, sodium carbonate, sodium hydroxide, etc

(Prestigiacomio et al., 2021; Ross et al., 2010; Sudibyo, Pecchi, & Tester, 2022). Certainly, such acid and based catalytic reactions depend on the nature of the feedstock. For manure as a biomass feedstock, there have been studies studying the effect of acid catalysts on the oil yield and composition (Liu et al., 2022; Posmanik et al., 2018). For example, Posmanik et al. showed how the addition of an acid catalyst (phosphoric acid) significantly improved the oil yield by 59% compared to without a catalyst (Posmanik et al., 2018). Similarly, Sudibyo et al. showed an improvement in oil yields for anaerobic digestates with acetic acid as a catalyst and also studied how low pH can achieve a lower %N in the oil improving its quality (Sudibyo, Pecchi, & Tester, 2022). An acetic acid-catalyzed HTL study done on algae by Yang et al. also showed an improved HHV for the bio-oil (W. Yang et al., 2017).

In this study, we use acetic acid as a reusable homogeneous catalyst since a previous study (Silva Thomsen et al., 2022) shows its potential recovery from HTL aqueous phase using and oxidation process. In this study, acetic acid is incorporated in the second stage of the two-stage process to identify any improvements in yield as evident from previous studies. Further investigation is performed to look at the reaction mechanisms and elemental composition changes due to changes in pH. To the best of our knowledge, this study would be first to utilize an acetic acid catalyst for the hydrothermal treatment of chicken manure to examine its effectiveness to enhance the quantitative and qualitative characteristics of the bio-oil. A comparison will be drawn for the biocrude oil produced in the second stage to compare results with and without the addition of the catalyst.

CHAPTER 3

RESEARCH MOTIVATION AND OBJECTIVE

3.1. Motivation for Research

As the global population grows, there is an increased need for more food supply. This increases the production of food and agricultural waste, posing a major challenge for waste management. The global food waste generated is 1.3 billion tons per year (Food and Agriculture Organization (FAO) of the United Nations. Food Wastage Footprint Impacts on Natural Resources; FAO: 2013) and in the U.S. alone the amount of waste generated from the dairy industry is 19 million tons annually (NRDC. Wasted: How America Is Losing Up to 40% of Its Food from Farm to Fork to Landfill; NRDC: New York, NY, 2012). The majority of these wastes are disposed of in landfills responsible for significant methane emissions in U.S (Hockstad, L., 2018). A common way to convert waste to energy is through the commercial route of producing biogas through anaerobic digestion. However, biogas only generates 40-50% yield leading to excess liquid effluent containing a mixture of nutrients and minerals (Déniel et al., 2016; Pham et al., 2015). Such high moisture content in effluents and wastes makes thermochemical processes like pyrolysis less suitable for recovery energy and nutrient-rich products.

Hydrothermal treatments like Hydrothermal Liquefaction (HTL) and Hydrothermal Carbonization (HTC) have shown promise in valorizing wet biomass feedstocks into valuable products (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Gupta et al., 2020; L. Li et al., 2013; J. Lu, Li, et al., 2018; Saqib et al., 2019; Tradler et al., 2018). Energy-rich biocrude oil, being the desired product from HTL, contains more nitrogen and oxygen content than typical petroleum crude oil. Such an increase is attributed to the

nitrogen and oxygen in wet biomass feedstocks like food waste or manure (Motavaf et al., 2022; Posmanik et al., 2018). This results in biocrude oils giving undesirable properties mainly lower heating value (Elliott et al., 2013; Montero-Hidalgo et al., 2019). There are ways to partition N into the aqueous phase solution (Y. Lu et al., 2015; Motavaf et al., 2021) resulting in bio-oil with reduced N and O content. On the other hand, N in the aqueous phase is seen as nutrient-rich that can be recovered as a fertilizer (Sudibyo, Pecchi, Harwood, et al., 2022). A way to look is to produce bio-crude oil with lower N content and at the same time produce a liquid stream with higher N recovery so that energy and nutrient-rich products can be recovered out of the hydrothermal treatments. HTC occurs at low temperatures (160°C-250°C) producing hydrochar as a solid product and aqueous solution (Kantarli et al., 2016; Pecchi et al., 2022; Zhou et al., 2019). HTC is demonstrated to partition N into an aqueous phase to generate Nitrogen-rich liquid stream (Costanzo et al., 2015; Motavaf et al., 2021). This HTC can be used as a pretreatment step and then perform HTL of the hydrochar produced to get bio-crude oil with less N and O content. Several studies are also performed to look at this two-stage hydrothermal process coupling HTC with HTL where feedstock is first treated with low temperatures and then the solid product undergoes liquefaction at higher temperatures to get bio-oil (Chakraborty et al., 2012; Jazrawi et al., 2015). In another study involving simulated food waste, Savage et al. used a two-stage hydrothermal process showing the highest N recovery (75%) in the aqueous phase and more than 50% in energy recovery for biocrude oil (Motavaf et al., 2022). Such a dual process showed evidence of better bio-oil quality, but since it is a two-stage process the oil yield will be less w.r.t feedstock. Process conditions including reaction temperature, time, and pressure can be optimized to look at the better quantity and quality of bio-oil (Sudibyo et al., 2021). More importantly, the pH of the reaction also plays a key role in

optimizing the oil yield and decreasing the N and O content (Posmanik et al., 2018; Sudibyo & Tester, 2023). HTL under acidic and basic leads to different mechanisms that have significantly impacted the yield and quality of bio-oil (Sudibyo, Pecchi, & Tester, 2022).

3.2. Research Objective

The objective of this study is to improve the quality of the biocrude oils that can be generated from hydrothermal liquefaction of wet wastes. Having a better quality for the biocrude oil makes it dispatchable as a drop-in fuel since it will have HHV close to petroleum crude oil. Such an objective is attainable by looking at two-stage hydrothermal liquefaction process to partition the nutrients into the aqueous phase and generate biocrude oils with higher %C and %H recovery resulting in better HHVs. In this study, chicken manure is used as the feedstock performing the two-stage HTC-HTL process and tuning the operating parameters to optimize boil-oil yield and quality. In addition, acetic acid is used here as a reusable catalyst to modulate the pH of the solution. Acetic acid is shown to be prominent and recoverable from the aqueous phase through thermochemical treatments (Silva Thomsen et al., 2022). A mechanistic study is also performed to improve understanding of the bio-oil formation by looking at the reaction mechanisms under different operating conditions that result in higher yield and less N and O content in biocrude-oil. For comparison, direct HTL of chicken manure is also performed to refer to the two-stage process. This study, to the best of our knowledge, is the first finding for the two-stage acid-catalyzed hydrothermal treatment of chicken manure.

The two-stage process will be conducted by first performing first step at low temperatures (160-250°C) hydrothermal carbonization of chicken manure for maximum removal of Nitrogen into the aqueous phase. This will be followed by higher temperature (250-350°C) hydrothermal liquefaction of the stage-1 hydrochar. To understand %C and %N recovery in all the three phases, elemental composition of solid, oil and aqueous products will be performed using elemental analyzers. Finally, to understand the underlying mechanism with pH and temperature severity, biocrude oil compound characterization is to be performed to deduce reaction pathways. This provides a model with optimized parameters and an understanding of the key reaction mechanisms that come into play during the hydrothermal treatment processes.

CHAPTER 4

MATERIALS AND METHODS

4.1. Materials

Chicken Manure (CM) was obtained from Cornell University Poultry Farmhouse Facility located in the town of Ithaca. This feedstock does not have any bedding or shed feathers present. CM was dried in an oven followed by grinding in ball-mill equipment to make a powdered mixture. DI water is used as a solvent. ACS-grade (Fisher Chemical) Acetone, dichloromethane, and ethyl acetate were used for the extraction of biocrude oil. Anhydrous MgSO_4 (Santa Cruz Biotechnology) is used for the removal of water from the biocrude oil-solvent mixture before extraction using a rotary evaporator. Glacial Acetic Acid from Fischer Chemical is used as an acid catalyst to modulate pH.

4.2. Experimental Design

The experimental methodology mentioned here is similar to what our group performed in previous studies (Sudiby, Pecchi, & Tester, 2022; K. Wang et al., 2020). The hydrothermal reactor studied here is a 500ml Parr 4575 reactor equipped with a Parr 4878 controller to control temperature and stirrer speed (130rpm) as depicted in Fig 8.

Chicken Manure (CM) of 15 grams is fed to the reactor with 150 ml of DI water to maintain a 1:10



Figure 8 Hydrothermal Treatment Reactor Apparatus-Parr Reactor (Parr Instrument Company)

biomass/water ratio. The reactor is purged with N₂ gas thrice to displace the air inside and then sealed with N₂ gas at 300 psi and the reaction is performed at the desired temperature and reaction time. The reaction time starts once the targeted temperature has been reached. After the reaction time, to end the experiment, the reactor was quenched to room temperature by flowing cold water through the internal cooling coil of the reactor and sweeping air externally to fasten the cooling process. Each experimental condition is at least performed in duplicates. Separation of the different product phases depends on the type of process (HTC or HTL) used, which depends on the operating conditions. Figure 9 shows a schematic diagram of HTC and HTL product separation methods.

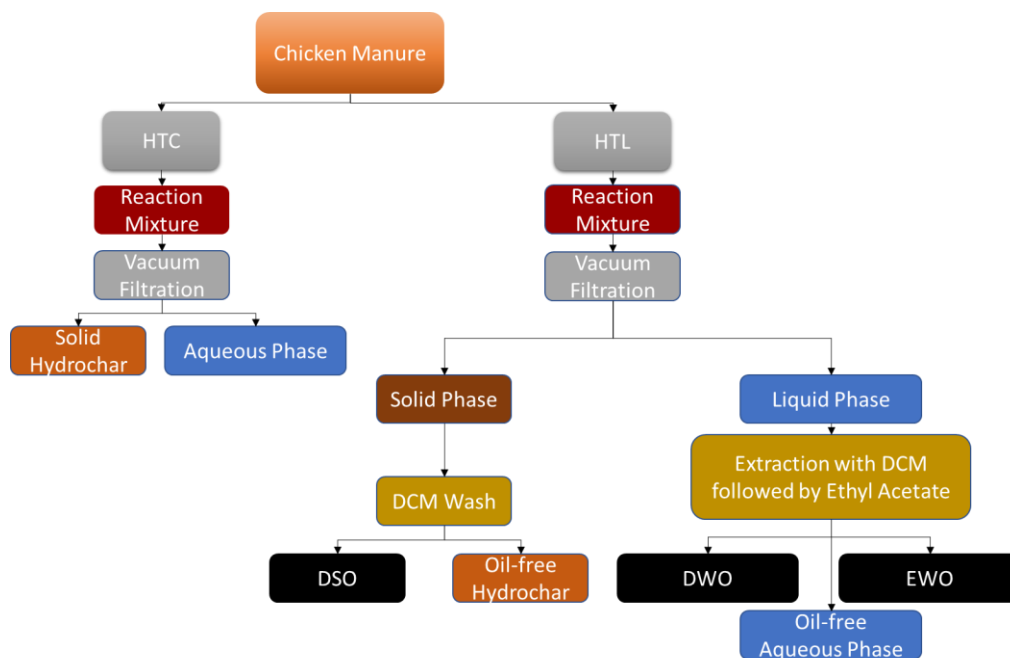


Figure 9 HTC and HTL Product Separation Methods

For Hydrothermal Carbonization (HTC), a solid phase (hydrochar) and an aqueous phase are formed apart from the gaseous phase which is vented after the reaction. The

two phases are separated by using vacuum filtration using a vacuum pump and dry cellulose filter paper. The liquid phase after weighing is immediately measured for pH. The solid phase collected after filtration is weighed with residual liquid present and kept in an oven at 105°C overnight to weigh the dry hydrochar the next day.

For Hydrothermal Liquefaction (HTL), four phases are formed: solid (hydrochar), oil (biocrude-oil), aqueous phase, and gas phase. Solid and liquid filtration is done with the same procedure as in the HTC process. Oil is bound to both solid and liquid phases separated. The liquid separated is collected and weighed, and immediately measured for pH. A part of the liquid is separated as a sample for liquid elemental and HPLC analysis. To extract oil from the remaining liquid, dichloromethane (DCM) is mixed in a 1:1 volume ratio, and the oil solubilized in DCM is separated from the aqueous phase using a separation funnel. This oil is termed here as DWO (DCM dissolved water-bound oil). To recover residual oil bound to the aqueous phase, ethyl acetate is used again in a 1:1 volume ratio with the aqueous phase. Oil dissolved in ethyl acetate is collected using a separation funnel and this oil is termed EWO (ethyl acetate dissolved water-bound oil). The solid product obtained (hydrochar) is washed with DCM and vacuum filtered to collect DCM-dissolved solid-bound oil (DSO).

DSO, DWO, and EWO collected samples are run through a rotary evaporator at 50°C and 80°C to separate and recover the solvents and collect solvent-free oils. DSO, DWO, and EWO solvent-free samples are left for drying for a couple of days for complete vaporization of DCM and ethyl acetate before weighing for oil yield and utilizing these samples for elemental and GC-MS analysis. The solid product is similarly dried using an oven at 105°C as in the HTC process to remove any bound DCM and weighed. A part of the aqueous phase collected for analysis is accounting for oil yield evaluations.

4.3. Analysis

The yields of hydrochar and biocrude oil were calculated using eq. 1. For HTC, only hydrochar will be evaluated from the below equations since no bio-oil is extracted.

$$Yield_i = \frac{m_i}{m_{CM}} \times 100\% \quad (1)$$

Where Yield is the yield of the product (wt basis), i is hydrochar or biocrude oil (HC/Oil), m_i is the respective product mass (g), and m_{CM} is the mass of dry chicken manure as feedstock (g). The total yield of oil is taken as the sum of the yields of the three biocrude oil fractions (DSO, DWO, and EWO).

Carbon, Hydrogen, and Nitrogen elemental composition in hydrochar and biocrude oil is obtained using CE-440 Elemental Analyzer (Exeter Analytical) using samples in triplicates (Appendix). Oxygen content in the hydrochar is estimated by using the difference method (%O= %Residue - %ash). Ash content (wt%) is determined following ASTM E1755-01 standard method (ASTM. Standard Test Method for Ash in Biomass. ASTM E1755-01, 2008; 545–545–3) . Sulfur is considered negligible for feedstock based on previous literature reporting of around 0.2-1% (wt%) for chicken manure (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Q. Li et al., 2021; Zhou et al., 2019). In this study for biocrude oils residual content is taken as the oxygen content since ash content in general is considered negligible for bio-oils (Posmanik et al., 2018).

Carbon yields in the biocrude oil and hydrochar were calculated using eq. 2.

$$C_{yield-i} = \frac{\%C_i \times m_i}{\%C_{CM} \times m_{CM}} \times 100\% \quad (2)$$

Where $C_{\text{yield-}i}$ denotes carbon yield in biocrude and hydrochar (wt basis), $\%C_i$ denotes carbon content in biocrude and hydrochar (wt%) similarly $\%C_{CM}$ denotes carbon content in CM (wt%). m_i is the respective product mass (g), and m_{CM} is the mass of dry chicken manure (g).

Similarly, nitrogen yields in hydrochar and biocrude oil are estimated the same as in eq. 2 with %N content in product and chicken manure as shown in eq. 3.

$$N_{\text{yield-}i} = \frac{\%N_i \times m_i}{\%N_{CM} \times m_{CM}} \times 100\% \quad (3)$$

Where $N_{\text{yield-}i}$ denotes N-yield in biocrude and hydrochar (wt basis), $\%N_i$ denotes nitrogen content in bio-oil and hydrochar (wt%) similarly $\%N_{CM}$ denotes nitrogen content in CM (wt%). Total carbon and nitrogen yield in bio-oil ($C_{\text{yield-oil}}$ and $N_{\text{yield-oil}}$) was taken as the sum of C & N yields of the three fractions of biocrude oil.

Total Organic Carbon (TOC_{LP}) and Total Nitrogen (TN_{LP}) concentration (g/L) in the liquid product were measured using an automated Shimadzu TOC-L and TNM-L analyzer (Appendix). Calculations for carbon and nitrogen yield in the aqueous phase vary for HTC and HTL processes. Liquid Products collected separately from HTL processes also contain residual oil (water-bound biocrude) that will be accounted for in the yield calculations. The original liquid product is used and not the aqueous phase after oil extraction in TOC and TN analyzers to prevent contamination and noise values due to DCM presence. Notice, the liquid product (LP) mentioned in this study is the original liquid with water-bound oil present in it whereas the aqueous phase (AP) mentioned in this study denotes oil-free liquid from the HTL process. Such a distinction will not exist for the HTC process.

Carbon and Nitrogen yields in the aqueous phase for the HTC process are estimated as shown in eq. 4 and eq. 5. From the %C and %N yield in the aqueous phase we can get the yields in the gas phase from eq. 6 and 7. Gas mass yields are estimated by taking the assumption that most of the gas is composed of CO₂ (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Sudibyo et al., 2021). The gas yield is then estimated by using eq. 8. From the hydrochar (HC) and gas yields, aqueous phase (AP) yields are estimated with eq. 9.

$$C_{yield-AP} = \frac{TOC_{AP} \times V_{AP}}{C_{feedstock}} \times 100\% \quad (4)$$

$$N_{yield-AP} = \frac{TN_{AP} \times V_{AP}}{N_{feedstock}} \times 100\% \quad (5)$$

$$C_{yield-gas} = 100\% - C_{yield-AP} - C_{yield-HC} \quad (6)$$

$$N_{yield-gas} = 100\% - N_{yield-AP} - N_{yield-HC} \quad (7)$$

$$Yield_{gas} = \frac{\left(\frac{44}{12}\right) \times C_{yield-gas} \times C_{feedstock}}{m_{feedstock}} \times 100\% \quad (8)$$

$$Yield_{AP} = 100\% - Yield_{HC} - Yield_{Gas} \quad (9)$$

Carbon and Nitrogen Yields for the Aqueous Phase for HTL process requires slight modification from the above equations as mentioned before because the liquid product also contains water-bound oil that needs to account in the equation. The modified equations 10 and 11 depict the carbon and nitrogen yields of aqueous phase. Carbon and Nitrogen yields of DWO and EWO were estimated using eq. 2 and 3.

$$C_{yield-AP} = \frac{TOC_{AP} \times V_{AP}}{C_{feedstock}} \times 100\% - C_{yield-DWO} - C_{yield-EWO} \quad (10)$$

$$N_{yield-AP} = \frac{TN_{AP} \times V_{AP}}{N_{feedstock}} \times 100\% - N_{yield-DWO} - N_{yield-EWO} \quad (11)$$

To estimate the Carbon and Nitrogen gas yields, we use equations 6 and 7 with addition of carbon and nitrogen yields of oil as shown in eq. 12 and 13.

$$C_{yield-gas} = 100\% - C_{yield-AP} - C_{yield-HC} - C_{yield-oil} \quad (12)$$

$$N_{yield-gas} = 100\% - N_{yield-AP} - N_{yield-HC} - N_{yield-oil} \quad (13)$$

From the carbon yield in the gas phase, the mass yield of gas phase is estimated same as in equation 8 even for HTL process. To estimate the mass yield of aqueous phase (AP) for HTL process, equation 9 is modified with addition of mass yield of oil as shown below in eq. 14.

$$Yield_{AP} = 100\% - Yield_{HC} - Yield_{Gas} - Yield_{oil} \quad (14)$$

Higher Heating Value (HHV) of the biocrude oil is important in this study when looking at reduction in %N and %O in the biocrude oil. Hydrochar obtained from the hydrothermal treatments is also seen as a solid fuel but is not the objective of this study (Q. Li et al., 2021; Zhou et al., 2019). HHV's of the bio-oils were estimated using equation 15 as mentioned before where Sulphur content and Ash content are omitted since they are negligible for biocrude-oils.

$$HHV \left(\frac{MJ}{kg} \right) = 0.3414C + 1.444S \left(H - \frac{N+O-1}{8} \right) \quad (15)$$

Lastly, Energy Recovery for oil also becomes an important factor (ER_{oil}) to be measured when looking from feedstock point of view which was estimated using equation 16.

$$ER_{oil} = \frac{m_{oil} \times HHV_{oil}}{m_{feedstock} \times HHV_{feedstock}} \times 100\% \quad (16)$$

CHAPTER 5

RESULTS AND DISCUSSION

This section is divided into three parts: Yields, Biocrude Oil Composition, and Aqueous Phase Composition. Each part is further explained detailing all the results obtained including product and carbon & nitrogen yields, elemental and compound characterization of both oil and aqueous phases through experiments performed. Also deducing the reaction mechanism and the reasoning behind the process pathway and respective yields and compounds estimated in the products.

5.1. Yields

As mentioned in the previous chapters, the yields estimated and discussed in this study are all w.r.t a dry feedstock mass basis. All the results produced are at least in duplicate with Base-Case (BC) experimental runs performed in triplicates. Yields mentioned in this study are not on an ash-free basis since the primary focus of this study is improving the quality of bio-crude oil (bio-oils have negligible ash content). As mentioned previously in the experimental design, the measurements are done right after the experiments, and on a consecutive day for moisture-free weight measurements after oven drying. Biomass: Water ratio is maintained at 1:10 in all the experiments. The sub-sections in each will be discussed in the following order: Base Case (BC), Two-Stage (TS): Stage-1, and Stage-2.

5.1.1. Product Yields

Base-Case:

Product yields of all four phases are disclosed in Table 3 for Hydrothermal Liquefaction (HTL) of Chicken-Manure which is the Base-Case (BC) for the study. These yields from the base case will be used as a reference to be compared to the Two-Stage (TS) process.

Table 3 Products Yields from HTL of Chicken Manure (Base Case-BC)

HTL of Chicken Manure		Solid		Oil		Liquid		Gas	
Temperature	Reaction Time	Mean	SD	Mean	SD	Mean	SD	Mean	SD
250°C	30min	25.05	± 1.62	12.95	± 0.64	20.62	± 5.21	41.38	± 7.27
300°C		24.59	± 3.07	18.61	± 0.72	15.81	± 1.11	40.99	± 2.38
350°C		19.31	± 0.69	15.45	± 0.93	1.25	± 0.00	63.99	± 5.40

The biocrude oils from both Table 3 and Fig. 9 show a range from 13-18.6 wt.% with a maximum at a temperature of 300°C. Biocrude oils yield in this study is a combination of yields of DSO, DWO, and EWO. DSO was observed with the highest yield compared to the other two (Sudibyo et al., 2021; Sudibyo, Pecchi, & Tester, 2022; Sudibyo & Tester, 2023). These results agree with previous studies on hydrothermal treatment of poultry/chicken manure (Ekpo, Ross, Camargo-Valero, & Williams, 2016; J. Lu, Li, et al., 2018). The biocrude yields obtained are lower than in other studies involving swine/cattle manure (Posmanik et al., 2018; Xiu et al., 2010). In general, lower yields of biocrude oil can be attributed to the high ash content and the nature of the feedstocks (Chen et al., 2014).

As seen in Fig. 10 the base case conditions of, 300°C and 30min result in the maximum biocrude oil yield compared to higher temperatures of 250°C and 350°C. Such effects

of temperature and reaction time are in agreement with previous studies involving chicken manure (Ekpo, Ross, Camargo-Valero, & Williams, 2016; J. Lu, Li, et al., 2018). These earlier HTL studies exhibited similar trends where a higher biocrude oil yield was observed at 310°C compared to 340°C for 30 minutes of reaction time (J. Lu, Li, et al., 2018). The standard deviation depicted in the table and the figure is due to triplicates performed for each scenario mentioned.

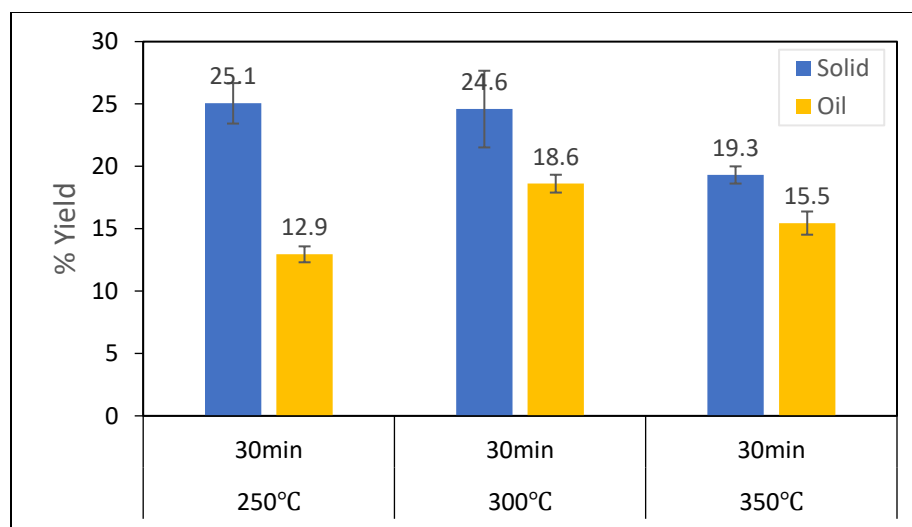


Figure 10 Hydrochar and Biocrude Oil Yields of HTL of Chicken Manure (BC)

Fig. 11 shows a complete yield balance of all four phases from HTL of Chicken Manure. The product yields of each phase are estimated by doing a complete carbon balance of the phases described in detail in the appendix to Chapter 4.

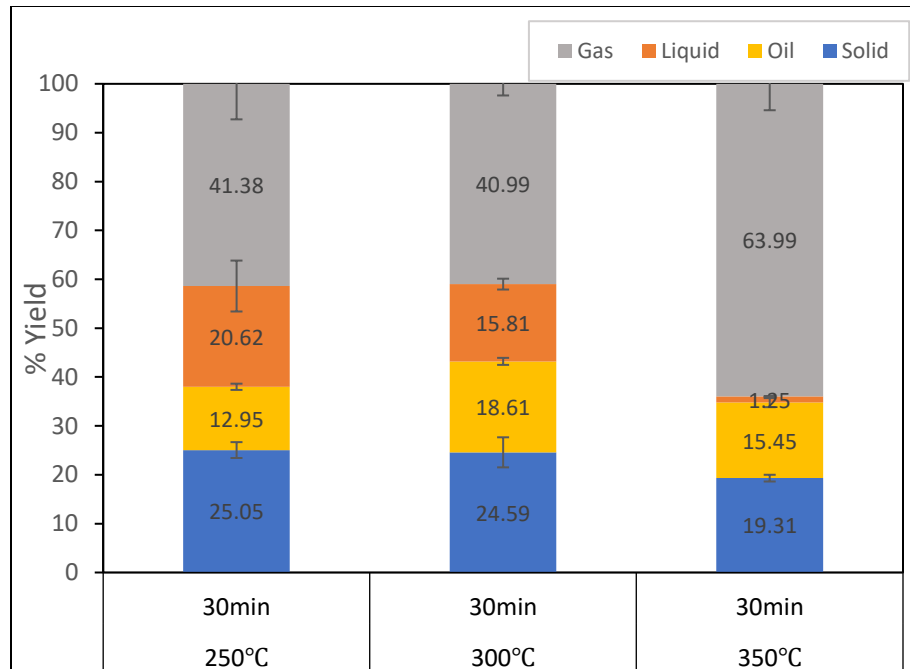


Figure 11 Yields of all four phases from HTL of Chicken Manure (BC)

Carbon recovery balance is done by using elemental composition data from the solid, oil, and aqueous phases (Appendx) (Sudibyo et al., 2021; Sudibyo, Pecchi, & Tester, 2022; Sudibyo & Tester, 2023). Fig. 10 shows more gas yield at high temperatures showing temperature severity on gasification. The gas yields are on a higher end compared to previous studies implying the possibility of different nature of the inorganics in the feedstock (J. Lu, Li, et al., 2018; Sudibyo, Pecchi, & Tester, 2022).

Stage-1:

Stage-1 of the Two-Stage process involves hydrothermal carbonization (HTC) of chicken manure. Low-temperature experiments are performed to partition nitrogen into the aqueous phase and then perform second stage HTL of the resultant hydrochar.

Table 4 Product Yields from HTC of Chicken Manure (Stage-1)

HTC of Chicken Manure		Liq		Gas		Solid	
Temperature	Reaction Time	Mean	SD	Mean	SD	Mean	SD
160°C	30min	45.60	± 1.53	0.00	± 0.00	54.40	± 2.17
	60min	42.42	± 1.13	0.00	± 0.00	57.58	± 1.60
190°C	30min	40.74	± 4.65	5.64	± 5.92	53.62	± 1.78
	60min	33.20	± 3.30	15.27	± 6.47	51.53	± 1.81
220°C	30min	35.10	± 1.38	18.79	± 2.32	46.11	± 0.95
	60min	35.64	± 1.98	18.34	± 2.51	46.03	± 0.53
250°C	30min	30.48	± 2.70	27.85	± 3.89	41.67	± 1.20
	60min	26.13	± 1.06	33.29	± 0.74	40.58	± 0.32

Table 4 and Fig. 12 show the product yield distribution for Hydrothermal Carbonization of CM (Stage-1) (Appendix). Figure 12 shows that low temperatures give higher yields of solid residue compared to higher temperatures. We see that the change in solid yields with reaction time is not as significant as with reaction temperature. This observation can be verified with a similar literature study on HTC of Chicken Manure varying between 30- and 60-minute reaction time (Kantarli et al., 2016; Lynam et al., 2015; Román et al., 2012). Many studies have also reported a similar trend for temperature severity (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Kantarli et al., 2016; Zhou et al., 2019). The low hydrochar yields at a high temperature are due to the decomposition of the solid undergoing liquefaction and gasification reactions giving rise to an increase in gas yield as shown in Fig. 12 (Kantarli et al., 2016; Pala et al., 2014). From these results, one would like to have a higher solid product yield to use the solid as a feedstock for HTL in the second stage. In this study, low temperatures like 160°C and 190°C show better solid yields and 30 minutes is a good reaction time since there is only a slight change at a longer reaction time (i.e., 60 minutes).

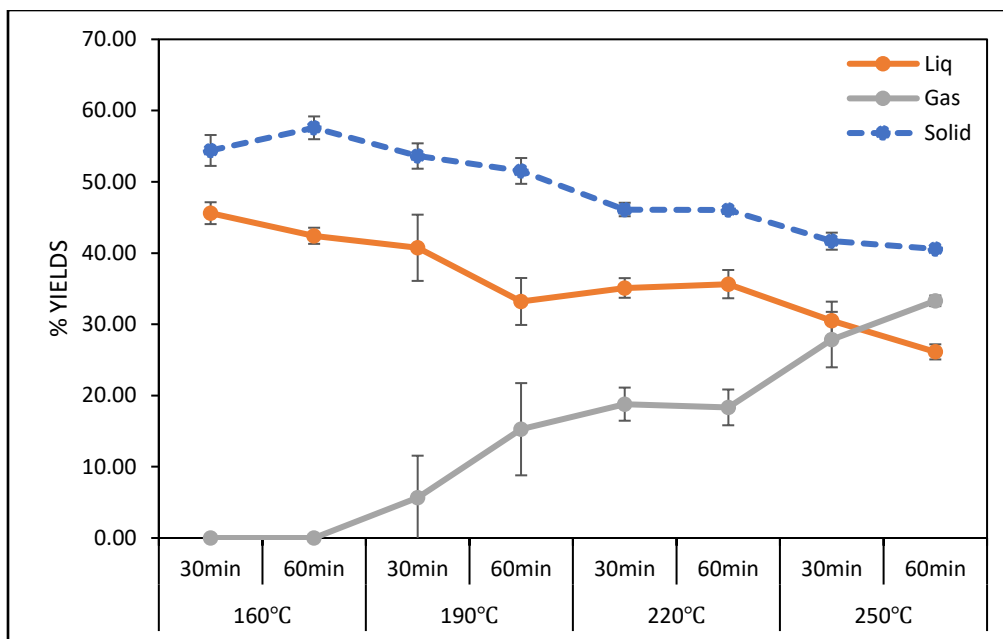


Figure 12 Products Yields from HTC of Chicken Manure (Stage-1)

Stage-2:

The second stage is performed by taking Hydrochar from Stage-1 as a feedstock. Table 5 and Figure 13 show the hydrochar (solid) and biocrude-oil yields for HTL of hydrochar produced from Stage-1. The yields are all w.r.t to the feedstock which was hydrochar from HTC of Chicken Manure under 190°C and 30 minutes. 190°C is chosen rather than 160°C to get hydrochar with a higher %C yield and lower %N yield. Further justification for choosing those parameters that are ideal for Stage-1 will be mentioned in later sub-sections (Carbon and Nitrogen Recovery/Yield).

Table 5 Stage-2 Solid and Oil Yields from HTL of Stage-1 Hydrochar (AA- Acetic Acid)

HTL of Stage-1 Hydrochar		Solid		Oil	
Temperature	Reaction	Mean	SD	Mean	SD
300°C	30min	38.16	± 4.09	13.55	± 1.75
300°C, 0.2M AA		43.13	± 0.25	19.99	± 0.94
350°C		40.15	± 0.42	16.08	± 0.31
350°C, 0.2M AA		41.52	± 0.64	16.54	± 0.14

250°C temperature is not performed in the two-stage process to reduce the number of experimental runs. Previous studies showed that lower the oil yields at 250°C. This result is reasonable given the proximity of reaction temperatures it to the transition between carbonization and liquefaction (Ekpo, Ross, Camargo-Valero, & Williams, 2016; Sudibyo et al., 2021). As shown in Table 5 and Figure 13, biocrude oil yields from the Two-Stage (TS) are higher at 300°C compared to 350°C. Such a decrease in biocrude oil yield can be attributed to decomposition associated with the production of more gas. This trend is also consistent with the Base-Case scenario previous studies (J. Lu, Li, et al., 2018; Sudibyo et al., 2021). Motavaf et al. also chose 300°C 30 minutes as optimal conditions for two-stage hydrothermal treatments of food waste (Motavaf et al., 2022).

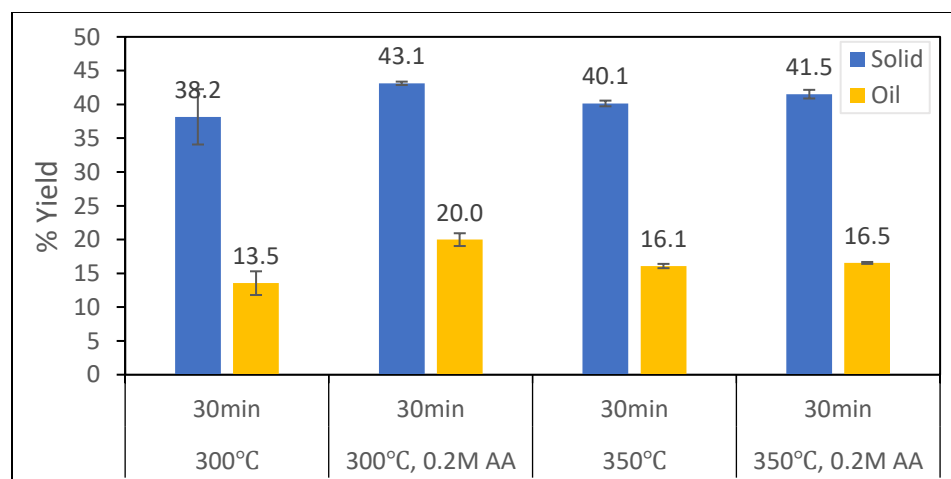


Figure 13 Stage-2 Solid and Oil Yields from HTL of Stage-1 Hydrochar (AA-Acetic Acid) (yields w.r.t hydrochar)

The yields are w.r.t hydrochar, the yields w.r.t chicken manure will be slightly greater than half of the values reported here. Since the hydrochar yield from Stage-1 is around 55 wt% for 190°C and 30 minutes from Table 4, this leads to a lower overall yield in

biocrude oil. Hence, pH is regulated in the second stage to look at improvements in biocrude oil yields. Silva Thomsen et al. reported that acetic acid can be seen as a potential carboxylic acid that can be recovered from the aqueous phase of hydrothermal liquefaction of sewage sludge (Silva Thomsen et al., 2022). Hence, acetic acid was used as a reusable catalyst in this study. From Figure 13, the addition of Acetic Acid increased the biocrude oil yield from 13.5 wt% to 20 wt%. Such an improvement under acidic pH conditions was also proven to increase biocrude oil yields from previous studies (Posmanik et al., 2018; Sudiby, Pecchi, & Tester, 2022).

0.2 M Acetic Acid addition caused this improvement, a specific distinction in pH variation for the base-case and two-stage process will be pointed out extensively in later sections. A point to be noted is that the addition of acetic acid does not have to be included in the feedstock basis for yield calculations. In a later section, it will be shown that acetic acid was not degraded, and excess was produced through aqueous phase characterization.

5.1.2. Carbon Yield/Recovery

All the results shown were evaluated by making use of the equations described in the Analysis sub-section and getting TN content from TOC/TN Elemental Analyzer (Appendix).

Base-Case:

Table 6 shows the %C recovery in each phase (solid, oil, liquid, and gas) from the feedstock after hydrothermal liquefaction at 250-350°C and 30 minutes. The same %C

recovery is also represented in Figure 13. As we see with the general mass yield balance of different products, the carbon yield for hydrochar decreases with an increase in temperature for HTL. Only a few studies previously have reported a complete carbon balance on hydrothermal liquefaction of poultry/chicken manure, they corroborate with the findings reported here on reduction in hydrochar yield with an increase in temperature (Ekpo, Ross, Camargo-Valero, & Williams, 2016; J. Lu, Li, et al., 2018).

Table 6 %C Recovery of Different Phases from HTL of Chicken Manure

%C Recovery		Solid		Oil		Liquid		Gas	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
250°C	30min	20.34	± 0.52	23.51	± 2.11	25.76	± 3.16	30.39	± 5.34
300°C		16.90	± 1.73	35.08	± 1.67	17.91	± 0.76	30.11	± 1.75
350°C		11.42	± 0.19	29.08	± 2.40	12.50	± 1.82	47.00	± 3.97

Figure 14 emphasizes %C recovery/yield in biocrude-oil since that is the primary focus of this study. From the figure we see a similar trend as with mass yields for biocrude oil, the optimum value is found at 300°C from the three temperatures. Lu et al. also performed a complete carbon balance on the four phases and reported a similar trend for hydrochar and biocrude oil, the %C recovery in biocrude oil was higher than in hydrochar (J. Lu, Li, et al., 2018).

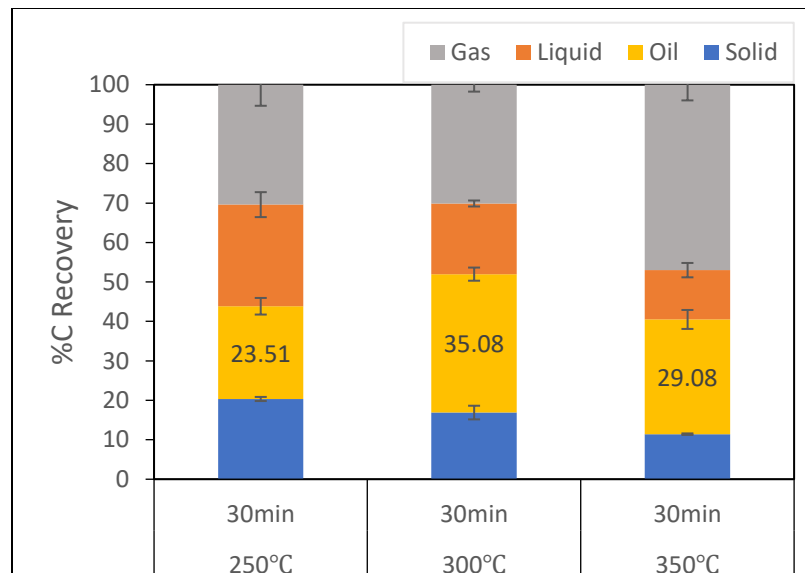


Figure 14 %C Recovery of Different Phases from HTL of Chicken Manure

Aqueous phase %C recover/yield is different from the previous literature on hydrothermal liquefaction of chicken manure (Ekpo, Ross, Camargo-Valero, & Williams, 2016; J. Lu, Li, et al., 2018). In this study we observed less C recovery in the aqueous phase and more in the gaseous phase. As mentioned before, these trends can be attributed to the physical and chemical characteristics of the feedstock including the inorganics in it (J. Lu, Li, et al., 2018; Sudibyoy, Pecchi, & Tester, 2022). Although not the focus of this study which aims to improve the biocrude oil quality, the changes in the distribution of carbon recovery among phases is a notable observation that is worthy of future investigation.

Stage-1:

For Stage-1, Table 7 and Figure 15 show the %C recovery/yield of the three phases (hydrochar, liquid, and gas) for hydrothermal carbonization of chicken manure at temperatures varying from 160°C to 250°C with reaction times of 30 and 60 minutes. For stage-1, we focus on the yields of hydrochar since that phase will be used

for the subsequent liquefaction step, hence the hydrochar %C recovery/yields are mentioned in particular in the figure. %C recovery/yield for hydrochar follows a slightly different trend from mass yields, there is a gradual increase in %C recovery from 160°C to 190°C and then a decrease in trend at a higher temperature which follows along with a decrease in the mass yield of hydrochar. This trend was also reported by Kantarli et al. of a slight increase and then a decrease in %C recovery for hydrothermal carbonization of poultry litter from 175°C to 250°C (Kantarli et al., 2016). Hence, in this study 190°C is found with a higher %C yield which is beneficial for the second stage of further processing. While 190°C processing resulted in lower hydrochar mass yields than observed at 160°C, the %N recovery should also be considered before choosing the optimal operating conditions.

Table 7 %C Recovery of Different Phases from HTC of Chicken Manure

%C Recovery		Liquid		Gas		Solid	
		Mean	SD	Mean	SD	Mean	SD
160°C	30min	47.05	± 1.50	0.18	± 0.18	53.93	± 0.16
	60min	45.54	± 0.38	1.56	± 0.81	52.90	± 0.43
190°C	30min	39.38	± 2.02	4.18	± 3.51	56.45	± 1.76
	60min	34.97	± 0.23	11.22	± 3.36	53.81	± 3.13
220°C	30min	37.35	± 0.19	13.80	± 1.21	48.85	± 1.01
	60min	38.00	± 0.89	13.47	± 1.30	48.54	± 0.41
250°C	30min	36.14	± 0.45	20.46	± 2.02	43.41	± 1.57
	60min	32.23	± 0.24	24.46	± 0.39	43.31	± 0.15

Kantarli et al. were among the few researchers who also reported complete %C recovery for all three phases with hydrothermal carbonization having poultry litter as feedstock (Kantarli et al., 2016). Kantarli et al. showed a decrease in %C yield in the aqueous phase and a simultaneous increase in %C yield in the gas phase as we increase the temperature from 175°C to 250°C with 30 minutes reaction time. Such a trend can also be found in Fig. 15 in this study where %C recovery in liquid decrease and an increase in the gas phase as we go from 160°C to 250°C for 30 minutes. This depicts the degradation of organics in the aqueous phase to the gas phase with an increase in temperature. It can be deduced that amino acids from the degradation of proteins in manure produce low-chain carboxylic acids in an aqueous solution under sub-critical water and on further degradation by decarboxylation produce gases (Kantarli et al., 2016; YANIK et al., 2007)

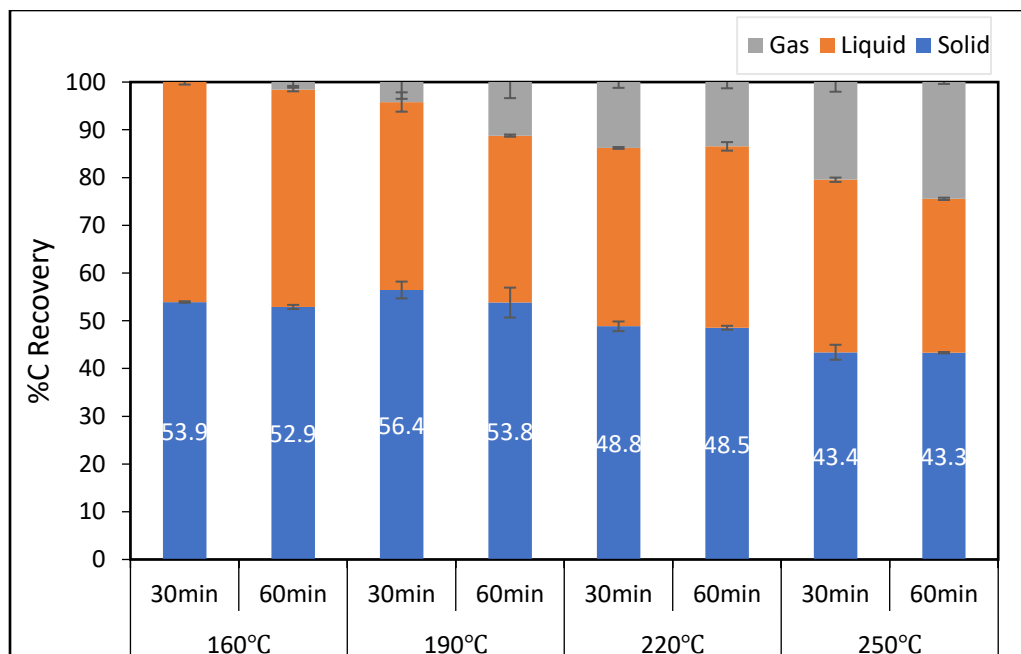


Figure 15 %C Recovery of Different Phases from HTC of Chicken Manure

Stage-2:

Stage-2 as mentioned before was performed by HTL of hydrochar produced in Stage-1. Hydrochar from Stage-1 is produced more to perform the second stage by choosing 190°C and 30 minutes as the operating conditions for max. mass yield of hydrochar and max. %C recovery with min. %N recovery. The basis for choosing these conditions as optimal will be discussed later in the %N recovery sub-section. The results shown in Fig. 16 depict the %C recovery/yields in hydrochar and bio-oil which are similar to the mass yields for Stage-2 discussed before where the addition of acetic acid led to increasing in biocrude-oil yield for 300°C operating temperature. These %C recovery/yields shown are w.r.t hydrochar from Stage-1 as were the previous results shown in Fig. 13.

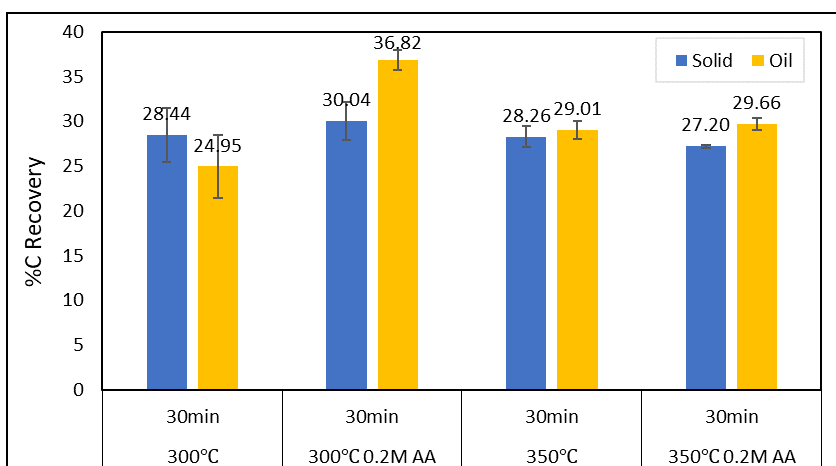


Figure 16 %C Recovery in Hydrochar and Biocrude-Oil (Stage-2)

To get a better picture it is good to just compare with one reference (feedstock) for %C recovery/yields. Fig. 17 shows the %C recovery in biocrude-oil from the feedstock (chicken manure) for Base-Case and from the Two-Stage process. From the figure, we see that even at optimal conditions for the Two-Stage process: 300°C and with 0.2 M

Acetic Acid (AA), we recover 20.8% carbon in bio-oil from the feedstock compared to 35% using single-stage conversion (Base-Case). However, nitrogen recovery is much less in the bio-crude oil improving its quality compared to direct HTL as mentioned in the next sub-section.

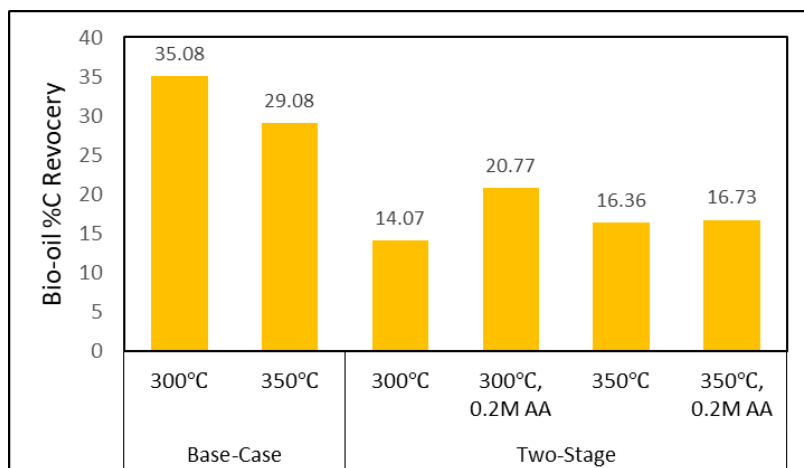


Figure 17 Total %C Recovery in Biocrude-Oil (Base-Case and Two-Stage)

5.1.3. Nitrogen Yield/Recovery

All the results shown were evaluated by making use of the equations described in the Analysis sub-section and getting TN content from TOC/TN Elemental Analyzer (Appendix).

Base-Case:

Similar to the %C recovery/yields in the previous section, one must also look at the %N recovery before deciding the optimized conditions for better quality and yield for the bio-oil. Table 8 and Figure 18 represent the %N recovery in different phases from HTL of Chicken Manure (Base-Case). From the Figure, it became evident that most of the

nitrogen was dispersed into the aqueous phase typically in ammonium or organic-N form (Matsumura et al., 2021). Such Nitrogen distribution can be supported by a previous study by Lu et al (J. Lu, Li, et al., 2018), where most of the nitrogen was partitioned into the aqueous phase followed by gas and oil phases with hydrochar having the least N-content. 300°C and 30 minutes was still considered the optimal condition for HTL in this case despite higher %N in bio-oil since more yield and %C recovery will offset this observation. While there is less N-content in biocrude-oil it still gave an oil with HHV of 32-33 MJ/kg as discussed in the following sub-section on biocrude-oil composition. Hence, it will be a good option to look at the bio-oil quality from the Two-Stage process and compare it with the Base-Case. The composition of the biocrude-oil will be discussed in detail to look at the Nitrogenous compounds present through GC-MS characterization.

Table 8 %N Recovery in Different Phases from HTL of Chicken Manure (Base-Case)

%N Recovery		Solid		Oil		Liquid		Gas	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
250°C	30min	16.82	± 0.66	18.84	± 1.34	41.39	± 5.15	22.95	± 3.64
300°C		12.54	± 1.59	22.91	± 0.68	43.57	± 4.18	20.97	± 3.46
350°C		10.01	± 3.68	19.20	± 1.20	40.96	± 5.44	29.83	± 3.92

The nature of the N-compounds i.e. either in ammonium or organic nitrogen form changes based on the reaction severity and feedstock characteristics. Interestingly, Ekpo et al. also found similar results where almost 50% of N-content was partitioned into the aqueous phase from hydrothermal treatment (at 250°C and 350°C) of Chicken manure

at 60 minutes reaction time (Ekpo, Ross, Camargo-Valero, & Williams, 2016). The N-content in the gas phase will be mostly in the form of NH₃ or NO_x, but they are negligible on a mass basis hence gas was considered completely CO₂ for all the yield calculations.

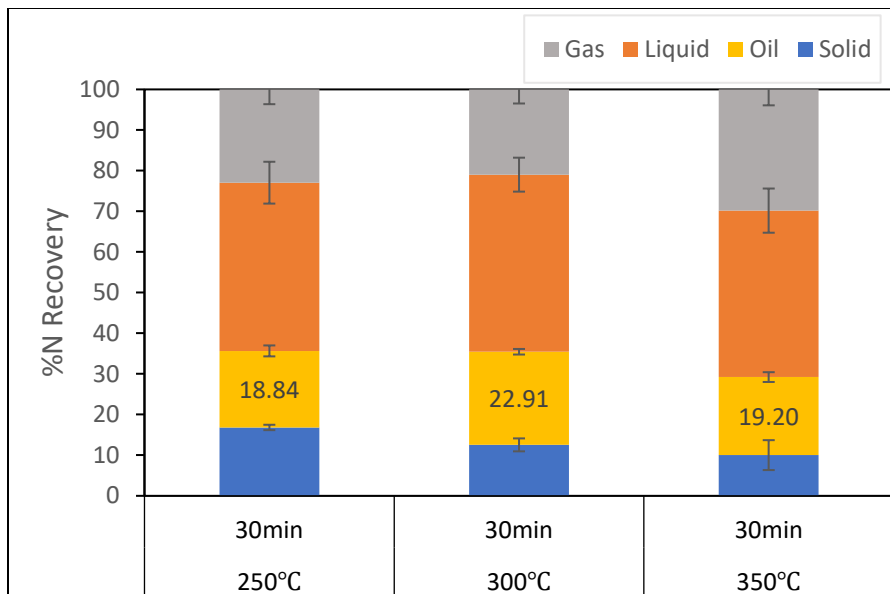


Figure 18 %N Recovery in Different Phases from HTL of Chicken Manure (Base-Case)

Stage-1:

For the Two-Stage process, HTC of Chicken Manure was performed as Stage-1, and Table 9 and Fig. 19 represent the %N distribution in the three phases of products obtained from Stage-1. From the Table and Figure, most of the Nitrogen was partitioned into the aqueous phase. While detailed discussion on N partition in different phases is still lacking in the literature, such a trend was also observed by Ekpo et al. where almost 60% Total-Nitrogen (TN) was partitioned into the aqueous phase on hydrothermal treatment of chicken manure at 170°C (Ekpo, Ross, Camargo-Valero, & Williams, 2016). The study also noted that most of the N-content was in organic-nitrogen form due to low-temperature severity.

Table 9 %N Recovery in Different Phases from HTC of Chicken Manure (Stage-1)

%N Recovery		Liq		Gas		Solid	
		Mean	SD	Mean	SD	Mean	SD
160°C	30min	53.23	± 2.77	4.51	± 0.00	42.26	± 0.80
	60min	50.22	± 0.10	9.81	± 0.33	39.97	± 0.43
190°C	30min	56.41	± 0.02	7.90	± 2.10	35.96	± 2.08
	60min	54.85	± 2.12	14.73	± 0.63	30.42	± 1.49
220°C	30min	61.98	± 0.91	8.35	± 1.35	29.68	± 0.43
	60min	62.74	± 0.61	7.40	± 0.43	29.87	± 0.18
250°C	30min	58.62	± 0.45	11.62	± 1.74	29.76	± 1.29
	60min	56.91	± 0.05	14.33	± 0.07	28.75	± 0.02

Mau et al. results were a contrast to this study, where most of the N-content was partitioned to hydrochar (70-90%) on HTC of Chicken Litter(Mau et al., 2016). Such a distinction can be attributed to different feedstock (chicken litter) and different operating parameters such as having a biomass/water ratio of 1:3 (this study used a 1:10 ratio). From Fig. 19, the %N content in hydrochar decreases with temperature severity which would be an ideal characteristic for using that hydrochar as feedstock for the second stage. The goal of Stage-1 was to get hydrochar with higher mass yield and %C recovery along with min. %N recovery. Among all 190°C was chosen as a better operating condition for Stage-1 since it also had more %C recovery and higher yield compared to temperatures at 220°C and 250°C. Between 30- and 60-minute reaction time, 30 min was chosen despite having a slightly higher %N content in hydrochar. This

was because most of the nitrogen was partitioned to the aqueous phase at 30 min compared to 60 min reaction time as shown in the Figure.

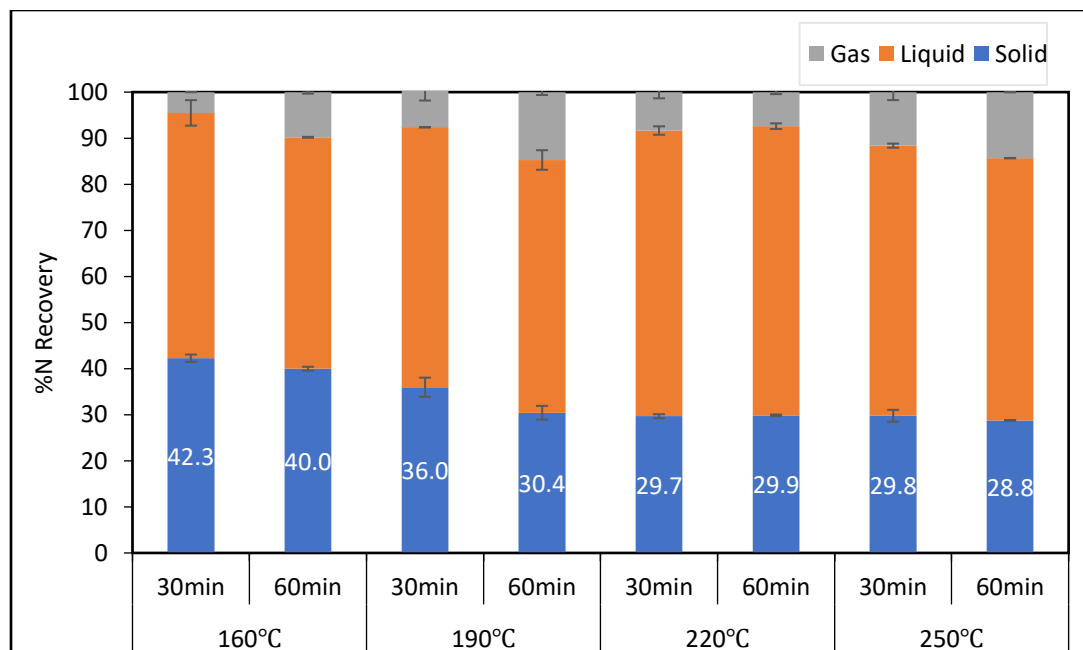


Figure 19 %N Recovery in Different Phases from HTC of Chicken Manure (Stage-1)

More N-content in the aqueous phase can be seen as a resource to recover as a nutrient-rich fertilizer (struvite) as shown in a previous study by Sudibyo et al (Sudibyo, Pecchi, Harwood, et al., 2022). Similarly, Motavaf et al. reported 200°C and 30 min as ideal conditions close to this study for maximum N recovery in the aqueous phase on HTC of simulated food wastes (Motavaf et al., 2021). Hence, for Stage-1 in this study, 190°C and 30 min were chosen as optimum conditions for obtaining hydrochar with higher yields and %C recovery and lower %N recovery to be utilized in the second stage HTL process.

Stage-2:

The results shown in Fig. 20 depict the %N recovery/yields in hydrochar and bio-oil from HTL of Stage-1 hydrochar. As mentioned previously, 190°C and 30 min was used as an optimum condition for Stage-1 to produce enough hydrochar through replicates. 300°C and 30 min with 0.2M Acetic Acid (AA) was chosen as a better optimal condition from Fig. 12 despite a slightly higher %N in bio-oil due to higher yield and %C recovery reported before at those operating conditions.

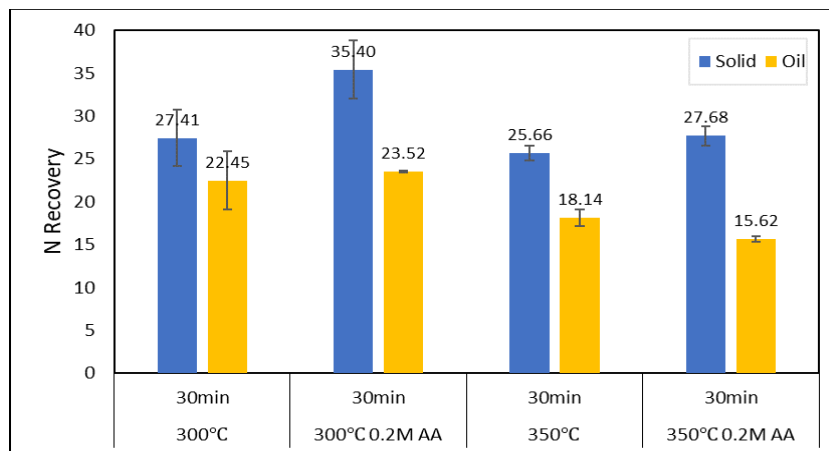


Figure 20 %N Recovery in Hydrochar and Biocrude Oil from HTL of Stage-1 Hydrochar

To compare the Base-Case and Two-Stage process for the %N recovery in the biocrude-oil we need to ensure that the reference is w.r.t the feedstock (chicken manure). Fig. 21 represents the comparison for %N recovery in biocrude-oil for both Base-Case and Two-Stage processes where we aim to get a low N-content in the biocrude-oil to improve its heating value. From the figure, since we consider 300°C as the ideal operating temperature condition, we observe 23% nitrogen recovery in bio-crude oil whereas from Two-Stage we get only 8.5% nitrogen recovery for 300°C with 0.2M Acetic Acid (AA) addition. Hence, despite a slight reduction in %C recovery in biocrude-oil in the Two-Stage process compared to Base-Case, we see a significant

reduction in %N recovery in the Two-Stage process. This also becomes evident from the next section describing the biocrude oil composition. Wu et al. and Motavaf et al. also have shown similar results with a significant reduction in %N in the bio-crude oil through a two-stage process on dairy manure and food waste (Motavaf et al., 2022; Wu et al., 2023). Their studies showed a reduction in %N in bio-oil to as low as 10-13% for the Two-Stage process with second stage HTL performed around 280°C-300°C and 30-60 min.

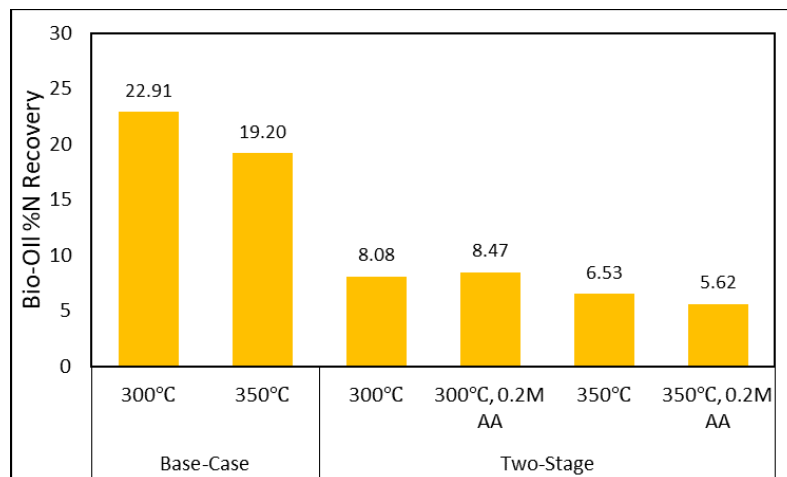


Figure 21 Total %N Recovery in Biocrude-Oil (Base-Case and Two-Stage)

5.2. Biocrude Oil Composition

The biocrude-oil composition gives many insights including the bio-oil quality, HHV, energy recovery from the feedstock, and reaction mechanism pathway. The Elemental composition of the biocrude-oil was estimated using CHN Elemental Analyzer (Appendix) by which HHV and Energy Recovery were estimated as mentioned in the

Analysis subsection. Getting elemental composition will help look at reaction mechanisms by making use of Van-Krevelen diagrams. Such mechanism pathways can be verified with the compound characterization of biocrude-oil using GC-MS (Appendix). This gives corroborated results when understanding the reactions governing the yield and quality of bio-oil.

5.2.1. Elemental Composition and Energy Recovery

The elemental composition and Higher Heating Values (HHVs) of biocrude-oils formed from HTL of different feedstocks taken from the literature are mentioned in Table 10. HTL parameters for the table data mentioned below can vary for different studies on temperature, reaction time, biomass/water ratio, etc. Table data gives a representative of typical HHV values in the literature of biocrude-oils produced from HTL of Manure feedstocks, we observe as noted before higher %N and %O leads to a decrease in the HHV. The Heating values taken from different literature were evaluated by the Dulong empirical formula (eq. 17).

$$HHV \left(\frac{MJ}{kg} \right) = 0.3383C + 1.422 \left(H - \frac{O}{8} \right) \quad (17)$$

Table 10 Elemental Composition and HHV of Bio-Oil from HTL of Manures from Literature

Feedstock	Biocrude Oil					Literature
	Ultimate Analysis				HHV (MJ/kg)	
	%C	%H	%N	%O		
Chicken Manure	71.6	7.8	4.8	16.8	32	This Study
	75.81	8.67	5.36	10.16	36.17	(J. Lu, Li, et al., 2018)
Dairy Manure	73	8	3.3	15.8	33.4	(Posmanik et al., 2018)
	67	8.1	3.2	21	28	(dos Passos et al., 2022)
Swine Manure	75.42	8.7	4.38	11.5	35.84	(J. Lu, Li, et al., 2018)
	75.02	8.14	4.87	11.97	34.83	(J. Lu, Watson, et al., 2018)

In this study, a HHV of 32 MJ/kg was observed for bio-oil from HTL of chicken manure at 300°C and 30-minute reaction time. Table 11 compares the composition and HHV of biocrude-oil from Base-Case and Two-Stage process. In this study, HHV was estimated using a modified Dulong-Berthelot equation (eq. 18) as mentioned earlier in the Analysis sub-section. Sulfur was omitted from the equation in our calculations due to negligible content for bio-oils from hydrothermal treatment of manures (0.2-1 wt%) (Ekpo, Ross, Camargo-Valero, & Fletcher, 2016; Q. Li et al., 2021; Motavaf et al., 2022).

$$HHV \left(\frac{MJ}{kg} \right) = 0.3414C + 1.4445 \left(H - \frac{N+O-1}{8} \right) + 0.093S \quad (18)$$

Table 11 Elemental Composition and HHV of Bio-Oils for Base-Case and Two-Stage

Bio-Oil	Base-Case			Two-Stage			
	250°C	300°C	350°C	300°C	300°C 0.2M AA	350°C	350°C 0.2M AA
%C	71.1	71.6	72.3	73.0	74.0	75.3	73.6
%H	8.6	7.8	8.1	9.6	10.1	10.3	10.2
%N	4.2	4.8	4.7	3.7	3.0	3.1	2.5
%O	16.1	16.8	15.2	13.7	12.9	11.3	13.7
HHV (MJ/kg)	33.3	32.0	33.1	35.9	37.2	38.2	37.2

Fig. 22 shows that HHV increased by about 4-5 MJ/kg with the Two-Stage process in comparison to crude oil (Cabrera et al., 2022).

Another observation from Table xxx that led to an increase in the HHVs was a decrease in %N and %O in bio-crude oils from the Two-Stage process compared to the Base-Case.

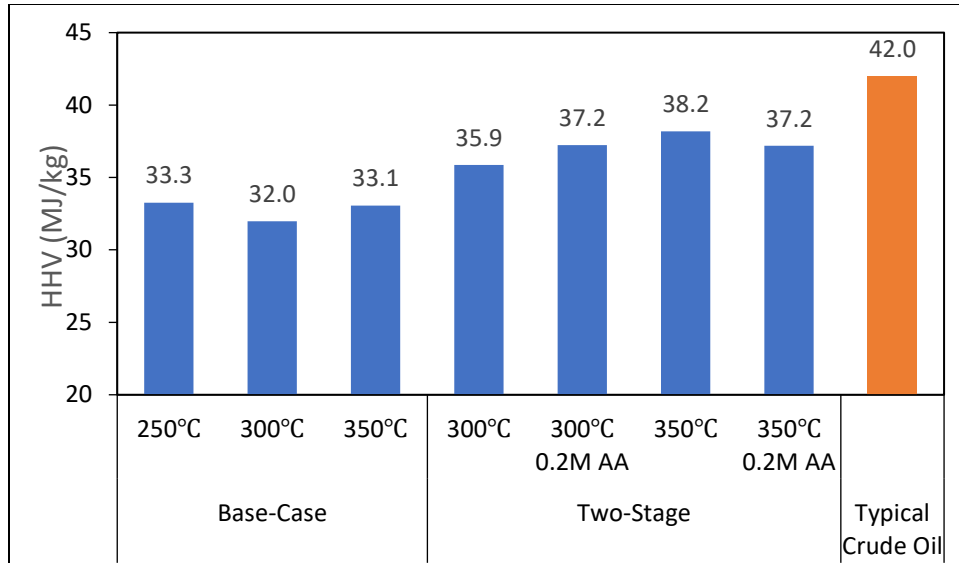


Figure 22 HHVs of Bio-Oils for Base-Case and Two-Stage

This result shows how N-partitioning into the aqueous phase and overall reduction in %N recovery in the bio-crude oil mentioned in the previous section played a role in the improvement in the quality of biocrude oil. A further improvement in %N decrease was seen with the addition of Acetic Acid (AA) in the Two-Stage process leading to an increase in HHV at 300°C. While at higher temperature severity (350°C), the addition of acetic acid catalyzed an increase in %O in the bio-oil which led to a slight decrease in HHV as shown in Fig. 21. Overall, we see an improvement in HHV by 15% from 32-33 MJ/kg (Base-Case) to 37-38 MJ/kg (Two-Stage).

While there was an improvement in HHV, one should also look at the energy recovery by producing bio-oils from chicken manure feedstock. Table 12 shows energy recovery by using eq. 19 which was also mentioned in the Analysis sub-section.

$$ER_{oil} = \frac{m_{oil} \times HHV_{oil}}{m_{feedstock} \times HHV_{feedstock}} \times 100\% \quad (19)$$

Table 12 Energy Recovery of Bio-oils from Chicken Manure Feedstock

Energy Recovery	Base-Case		Two-Stage			
	300°C	350°C	300°C	300°C, 0.2 M AA	350°C	350°C, 0.2M AA
bio-oil yield (wt%)	18.60	15.50	7.24	10.72	8.63	8.84
HHV of feedstock (g)	14.70	14.70	14.70	14.70	14.70	14.70
HHV of bio-oil (g)	32.00	33.10	35.90	37.20	38.20	37.20
Bio-Oil Energy Recovery (%)	40.49	34.90	17.67	27.13	22.43	22.38

We see a lower energy recovery in general due to lower oil yields with chicken manure as feedstock. The energy recoveries further decreased in the Two-Stage processes as this is due to lower bio-oil yields w.r.t chicken manure as feedstock. Since the yield of hydrochar from Stage-1 was around 53.6% for 190°C and 30 min from Table 4, this was adjusted to get bio-oil yields w.r.t chicken manure for the Two-Stage process.

5.2.2. Compound Characterization and Reaction Mechanism

As mentioned, all the compounds were characterized using GC-MS and grouped based on their functional groups. The groups shown in the graphs are Carboxylic Acids/Esters; Alcohols (mostly phenols); Ketones; Aliphatic Hydrocarbons; Nitrogen-Heterocyclics; Amides/Amines etc. Ethers and Aldehydes were also detected but due to negligible area% were not included in the graphs.

Base-Case:

Fig. 23 shows the compound groups observed in bio-oil produced from HTL of chicken manure (base-case). The areas of all the compound groups in Fig. 23 sum to >70% of the total area. What we observe from the figure was a decrease in carboxylic acids, this result was validated with a decrease in O/C ratio in the Van Krevelen diagram in Fig. 24. The removal of oxygen content in bio-oil occurs through decarboxylation or dehydration mechanisms (Peterson et al., 2008). Van Krevelen diagrams were all

prepared by making use of elemental composition shown in Table 11. More data points in Fig. 24 depict more replicates that show the dehydration mechanism.

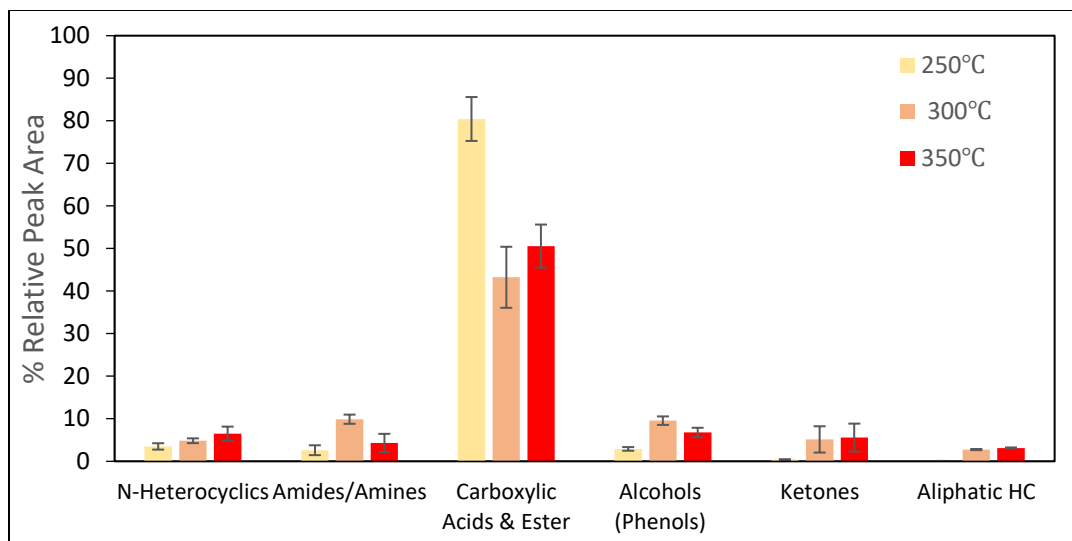


Figure 23 Bio-Oil Composition from HTL of Chicken Manure-Base Case (GC-MS)

The decrease in the O/C ratio in the bio-oil depicting deoxygenation is good for the bio-oil quality but a simultaneous decrease in the H/C ratio leads to lower HHV. A better outcome would be for a decrease in O/C and an increase in the H/C ratio (decarboxylation mechanism). Dehydration is the removal of oxygen as water whereas the decarboxylation mechanism is the removal of carbon dioxide. A reduction in the H/C ratio also means lower hydrocarbons as shown in Fig. 23. Only in the Base-Case HTL experiments were performed at 250°C were we see more carboxylic acids from GC-MS analysis. An increase in temperature from 250°C to 350°C led to a decrease in carboxylic acids, this result is consistent with the two-stage study performed by Motavaf et al. on food waste (Motavaf et al., 2022).

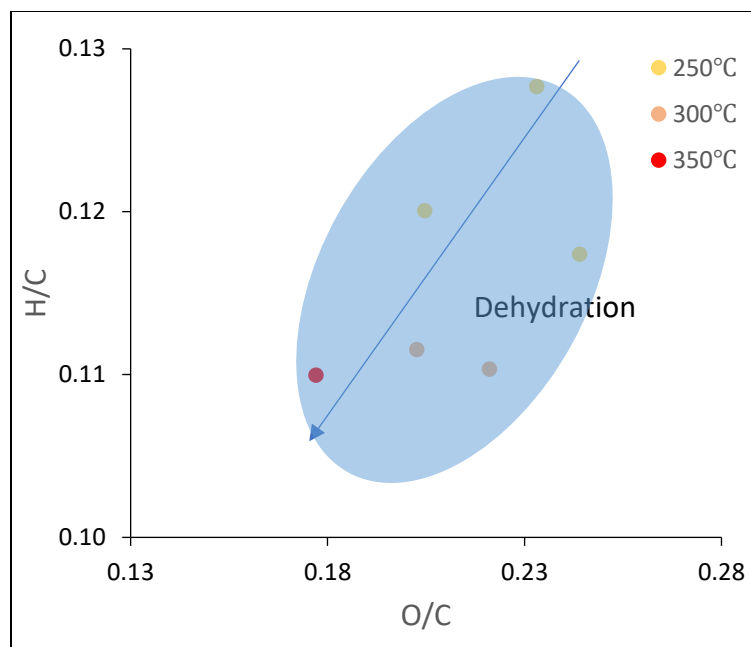


Figure 24 Van Krevelen Diagram showing the dehydration mechanism of bio-crude oil for the results obtained in this study

Two-Stage:

Figure 25 depicts the biocrude-oil compound characterization from the Two-Stage process and Fig. 26 represents the Van-Krevelen diagram prepared by using the elemental composition of the bio-crude oil. From the Van-Krevelen diagram, we can see a decrease in the O/C ratio and an increase in the H/C ratio. This effect was also confirmed by Fig. 25 which showed a decrease in carboxylic acids, an increase in temperature severity, and a noticeable increase in aliphatic hydrocarbons. These results indicate that the overall reaction undergoes decarboxylation, where oxygen is removed in the form of carbon dioxide (Posmanik et al., 2018) which improves the quality of the bio-crude oil compared to the dehydration reaction, as evident by the larger HHV (MJ/kg) (see Table 11). Another noticeable outcome from Fig. 25 is a significant

reduction in nitrogenous compounds in the presence of acetic acid as a catalyst and with temperature severity.

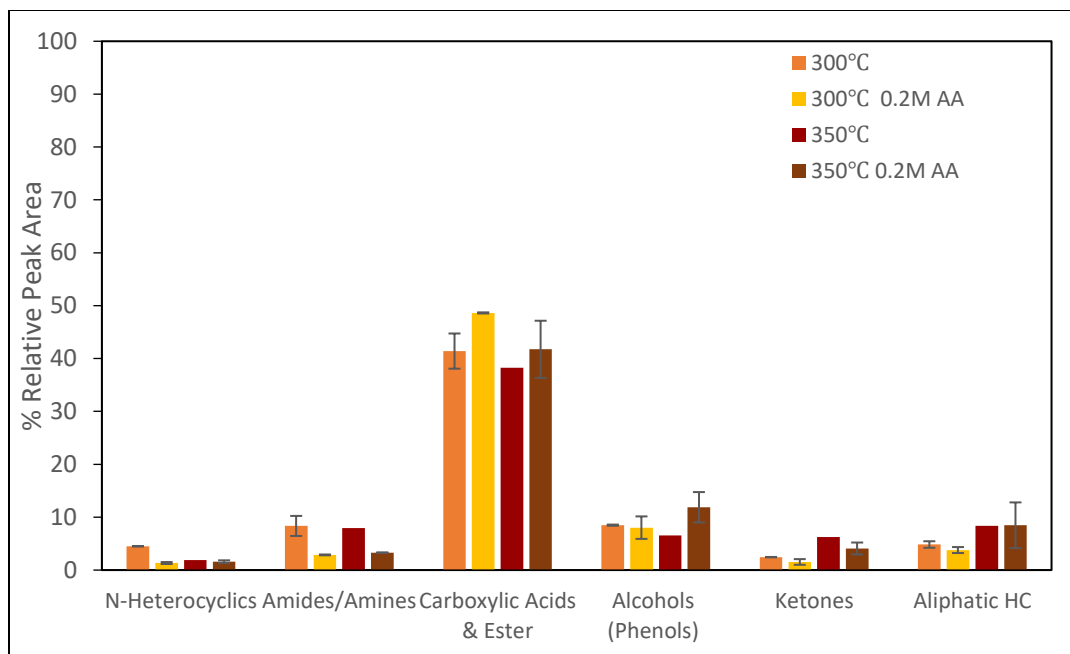


Figure 25 Bio-Crude Oil Composition from Two-Stage at 300°C and 350°C

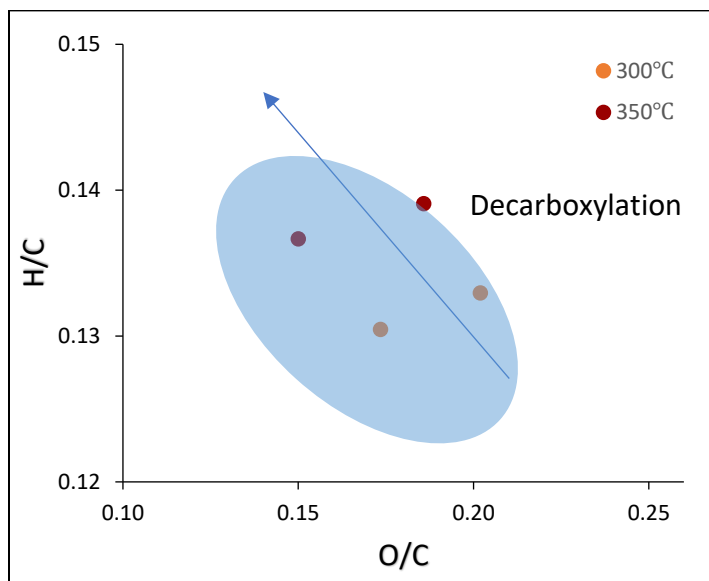


Figure 26 Van Krevelen Diagram showing the decarboxylation mechanism of bio-crude oil

From Fig. 25, we saw that an increase in temperature severity led to a reduction in N-heterocyclics in biocrude-oil from HTL of the Two-Stage process. This was also observed in previous studies by Sudibyoy and coworkers in our group where temperature severity led to denitrogenation with cleavage of the amino group into the aqueous phase (Sudibyoy, Pecchi, & Tester, 2022; Sudibyoy & Tester, 2023). Li et al. (2022) also identified that higher reaction severity leads to the removal of nitrogen in the form of NH_3 into the aqueous phase Fig. 27 validates the direct cleavage of the amino group with temperature severity, where an increase in temperature led to a reduction in N/C and an increase in H/C that favors bio-oil quality. However, such a trend was not observed for the base-case bio-oil temperature in this study and the reasoning for that is beyond the scope of this study.

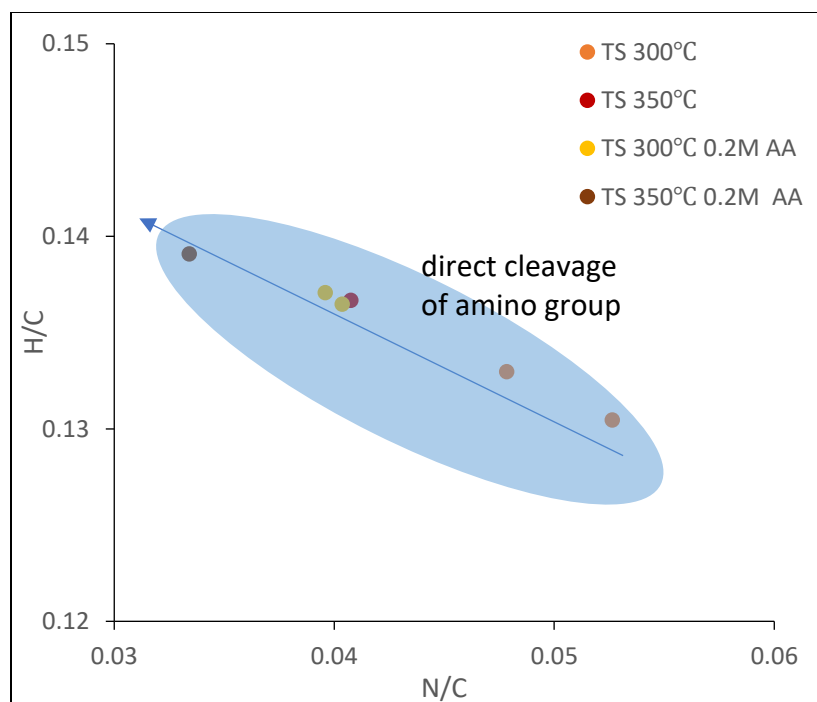


Figure 27 Van Krevelen Diagram showing the denitrogenation mechanism of bio-oil (TS-Two Stage, BC- Base Case)

An important characteristic observed is the role of pH compared to temperature severity in these studies. Compared to Base-Case (BC), there is a significant reduction in %N content in bio-oils from Two-Stage (TS), particularly for the case with the addition of 0.2 M Acetic Acid (AA). For the Two-Stage process, without acetic acid addition gave a pH of 7.5 for the second stage HTL aqueous solution whereas the addition of acetic acid led to a pH of 5.5 at 300°C operating temperature (Two Stage process occurring in acidic conditions under acetic acid). Base-Case HTL gave an alkaline solution (pH of 9 at 300°C operating condition) showing the basic nature of chicken manure (Base Case in alkaline conditions). GC-MS compound characterization and Van-Krevelen plots were plotted between base-case and two-stage process at 300°C and 350°C in the following figures to compare and show the pH role in %N content in bio-oils.

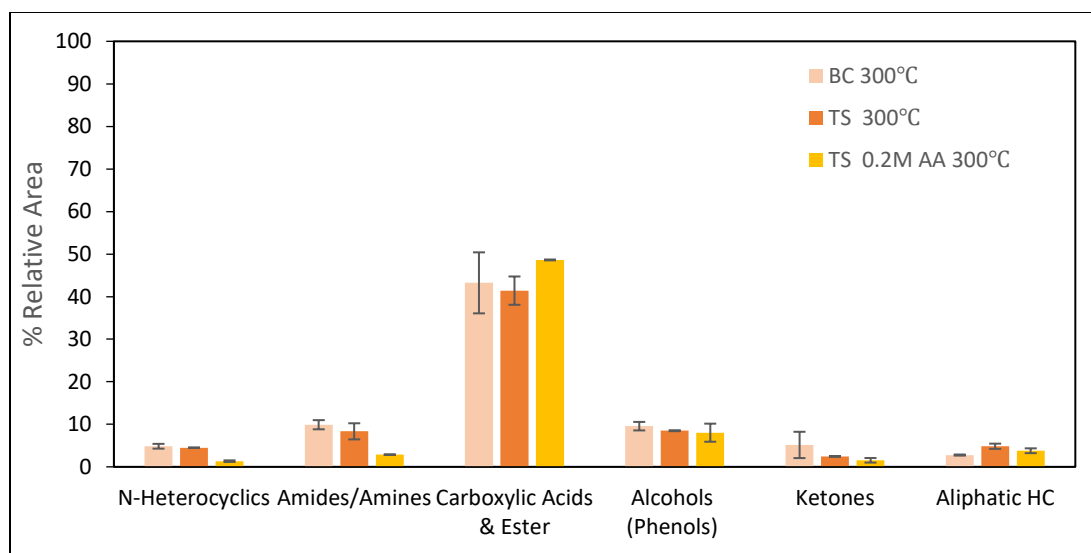


Figure 28 Bio-Crude Oil Composition from Base-Case and Two-Stage HTL at 300°C
(TS-Two Stage, BC- Base Case)

Fig. 28 shows the composition of bio-oils from HTL of Base-Case (BC) and Two-Stage (TS) including the addition of 0.2M acetic acid (AA). From the Fig, it becomes evident

that there was a significant reduction in %N content due to a decrease in N-heterocyclics and Amides/Amines, particularly in the case of Acetic Acid. Clearly, acidic pH reaction conditions for HTL favored a reduction in %N content in biocrude oil. Since Base-Case was HTL performed at alkaline conditions, a reaction pathway that is possible is the Maillard reaction. This reaction was shown before by Sudiby et al (Sudiby, Pecchi, & Tester, 2022) where through the alkaline pathway the degradation of cellulose produces carbonyl and hydroxy carbonyl reactive intermediates that enhance the degradation of amino acids and rearrangement of ammonia. Pyridines, Pyrazines, Pyrroles compounds, and their derivatives result from the Maillard reaction (N-heterocyclics). Having a low-pH reaction will limit Maillard's reaction and therefore leads to a reduction in %N in the bio-oil. The Base-Case had a higher %N content in the bio-oil evidenced by the GC-MS analysis and by the elemental composition shown before in Table 11.

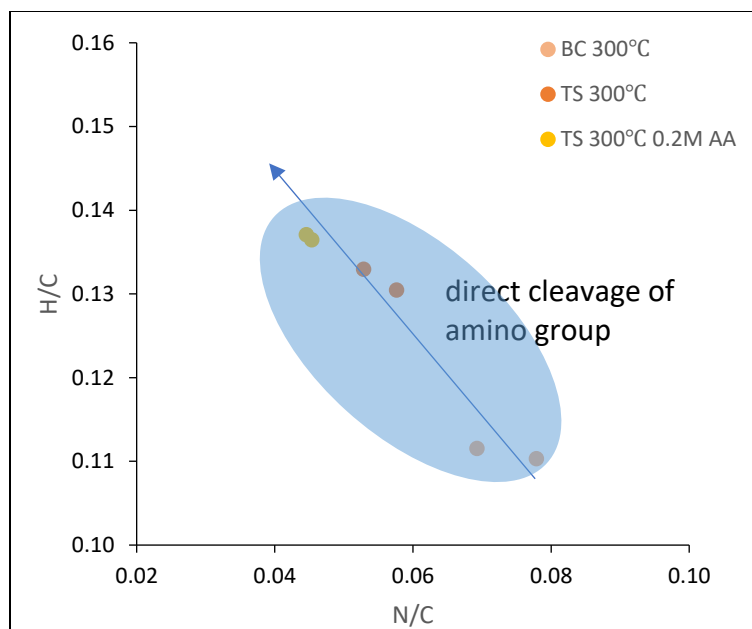


Figure 29 Van Krevelen Diagram showing direct amino group cleavage mechanism

Using the elemental composition table, Fig. 29 shows the comparison between base-case and two-stage for HTL at 300°C in a Van-Krevelen diagram. The mechanism follows direct cleavage of the amino group as shown before for temperature severity. Hence, acidic pH conditions enhance the deamination of amino groups and correspondingly result in nitrogen removal into the aqueous phase. Again, these observations can be supported in an earlier study in our group by Sudibyo and Tester (2023), where acetic acid addition led to increased deamination and an increase in nitrogen removal from biocrude oils. A combination of temperature severity and acidic condition caused a reduction in N/C and an increase in H/C, thereby increasing the total amount of hydrocarbons products. Fig. 30 and 31 show GC-MS compound characterization and Van-Krevelen diagrams for Base-Case and Two-Stage for HTL at 350°C. We see a higher hydrocarbon content following the deamination mechanism as shown by the Van-Krevelen diagram.

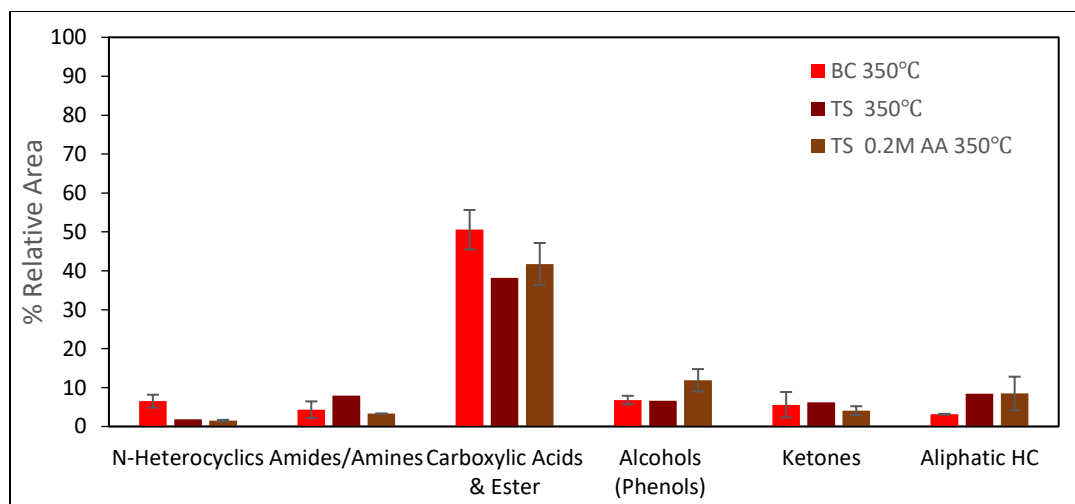


Figure 30 Bio-Crude Oil Composition from Base-Case and Two-Stage HTL at 350°C

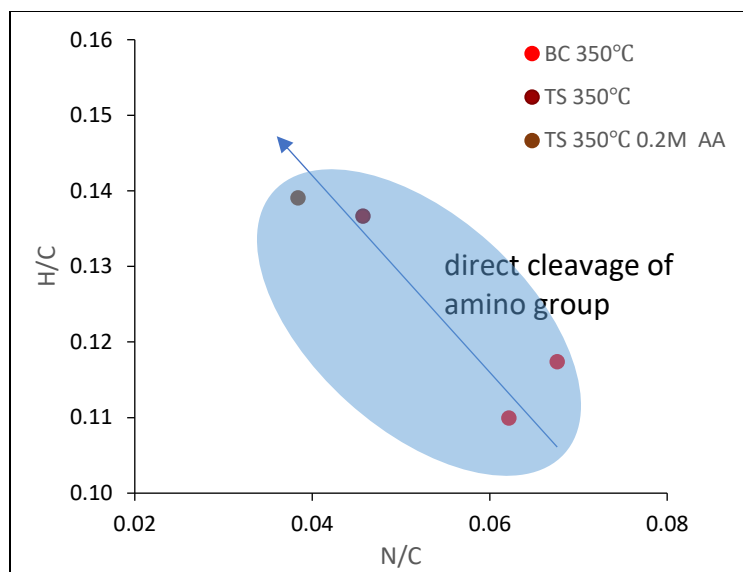


Figure 31 Van Krevelen Diagram showing direct amino group cleavage mechanism

While 350°C shows better results with higher temperature severity, choosing 300°C as the optimal temperature for a two-stage process was ideal due to higher bio-oil mass yields. The addition of acetic acid (0.2M) for the two-stage process at 300°C was chosen as the best scenario balancing mass, carbon, and nitrogen yields for the highest energy recovery in bio-oils and highest nutrient recovery in the aqueous phase.

5.3. Aqueous Phase Composition

The compound characterization of the aqueous phase utilized HPLC-UV analysis (Appendix). Concentrations were estimated by using standards (organic acids like acetic, lactic, and formic acid; 1,3- cyclopentanone, phenol, and its derivatives, etc.) as a reference. The important characteristic of compound characterization involved checking for the presence of acetic acid to validate the reusability of the acid as a homogeneous catalyst.

5.3.1. Presence of Acetic Acid

Acetic Acid (AA) was chosen as a homogeneous catalyst for the catalytic acid-based HTL reactions in the Two-Stage process in this study. Acetic acid was an attractive choice as a catalyst for hydrothermal treatment because of its potential to be reused. Fig. 32 shows the concentration of acetic acid detected in the aqueous phase from HTL experiments both in base-case and two-stage process. Acetic acid was produced in equal or more amounts to the acid added (0.2M) as shown in the Figure for 300°C and 350°C Two-Stage HTL.

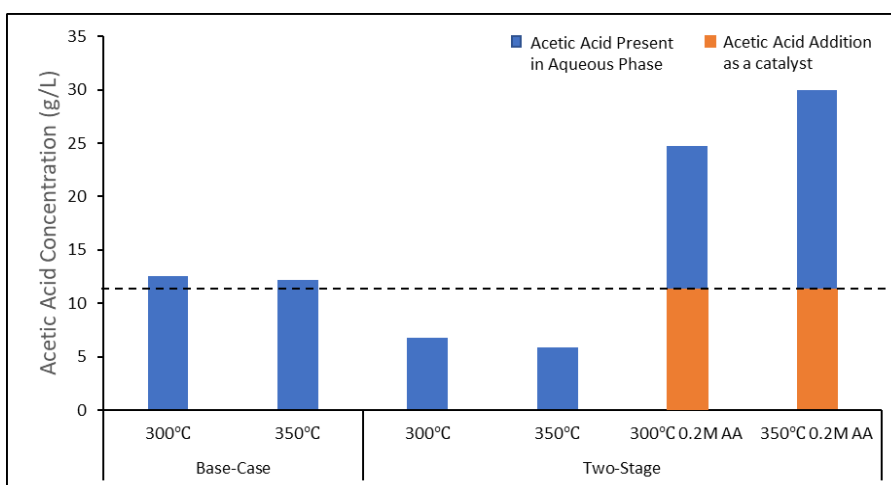


Figure 32 Acetic Acid Concentration in the Aqueous Phase of HT

5.3.2. Compounds Characterization

Other compounds with higher concentrations detected in the aqueous phase are formic acid, lactic acid, and 1,3- cyclopentanedione as shown in Fig. 33. Acetic acid was chosen in particular compared to other acids because of the ability to oxidize organic acids to acetic acid by wet oxidation of aqueous phase. Silva Thomsen et al. showed in their study on wet air oxidation of the aqueous phase from HTL of sewage sludge where organic compounds can be converted to acetic acid (Silva Thomsen et al., 2022). In

general, formic acid degrades acting as a hydrogen donor and lactic acid can undergo decarboxylation to acetaldehyde at higher temperature severity as observed in Fig. 33 (Sudibyo & Tester, 2023). Whereas acetic acid is relatively stable till 400°C making it ideal for reusability by making use of oxidative treatment for conversion of organic acids into acetic acid. Proving the extraction of acetic acid from the aqueous phase is beyond the scope of this study since the focus is on improving the quality of bio-oil through the two-stage hydrothermal treatment process.

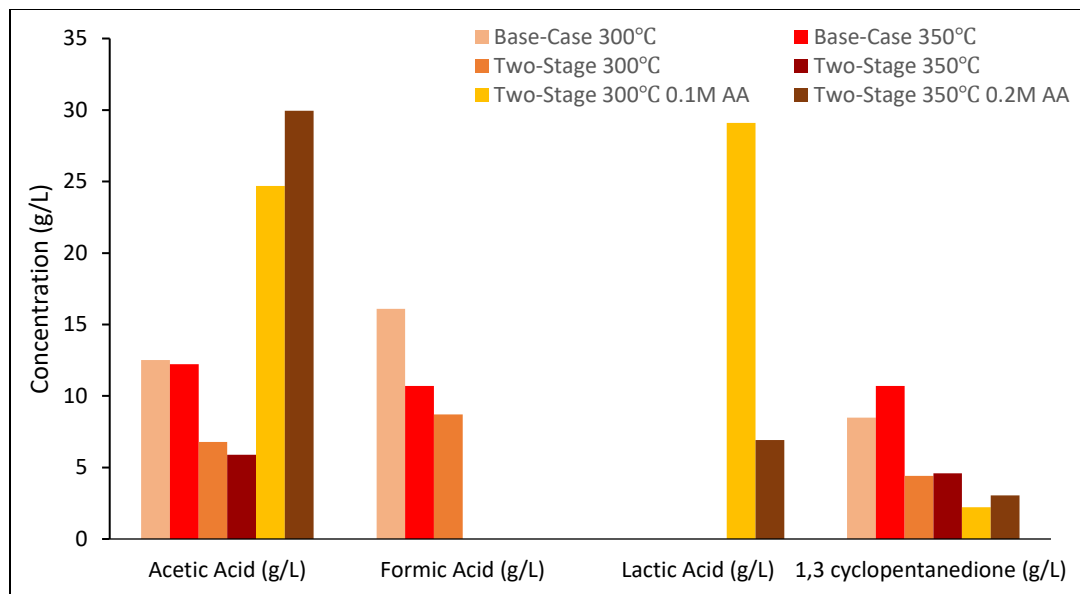


Figure 33 Other Major Organics Concentration in the Aqueous Phase of HTL

CHAPTER 6

IMPLICATIONS AND INFERENCE

Compared to commercially existing waste management techniques, we see hydrothermal processing as a promising method for valorizing wet waste streams like agricultural and food wastes. A key challenge is that biomass wet feedstocks contain higher impurities like nitrogen and oxygen making the biocrude-oil produced from the hydrothermal liquefaction less favorable in terms of lower heating value. For example, measurements carried out in this study of direct hydrothermal liquefaction of chicken manure led to the production of biocrude-oil products with HHVs of 32 to 33 MJ/kg compared to 42 to 44 MJ/kg characteristic of petroleum crude oil. While hydrothermal treatment seems promising in preventing methane emissions from direct landfill, the products produced from the waste valorization should be applicable for direct application as drop-in fuels/chemicals. This implies that the nitrogen and oxygen contents of produced bio-oils need to be lower.

Two-Stage hydrothermal processing of wet wastes is seen as a way to make biocrude-oils with higher heating value reach commercial-grade crude oil. In this study, the first stage was performed at a lower temperature to carbonize chicken manure feedstock and to partition nitrogen into the aqueous phase. From the results of this study, the hydrochar produced from the first stage had the highest carbon recovery (~56%) with min. nitrogen recovery (~36%) at 190°C and 30 minutes by optimizing operating conditions. This implies that having a lower/higher temperature and reaction time than that will not lead to optimized results for hydrochar mass yields, carbon, and nitrogen recovery. The

second stage experiments were performed at higher temperatures, where it was observed that reaction at 300°C for 30 min produced higher yields of biocrude-oil.

Choosing 190°C for the first stage and 300°C for the second stage with a 30-minute reaction time for both, we see a reduction in %N recovery and an improvement in mass and carbon yields in the biocrude oil from the two-stage process. The composition of the biocrude-oils also validates the improvement in the HHV from two-stage compared to the base-case scenario. While the two-stage process led to an improved bio-oil quality due to the maximum removal/portioning of nitrogen into the aqueous phase, it still leads to an overall lower bio-crude oil yield. Further improvement in bio-oil quality was shown by catalyzing the second stage HTL with the incorporation of acetic acid.

Two-Stage acid-catalyzed hydrothermal treatments were performed with the addition of acetic acid in the stage-2 HTL. We saw an improvement in bio-oil yields for 300°C HTL reaction with 0.2M acetic acid. In addition, there has also been an improvement in the biocrude-oil quality with a higher %C, %H, and a reduction in %N and %O content. Hence, we were able to achieve higher HHV of bio-crude oils from the two-stage acid-catalyzed process with values of 37-38 MJ/kg being closer to the 42 MJ/kg crude-oil benchmark. Understanding the mechanism for such an increase in the quality of bio-oil becomes important to infer more about the thermochemical reaction pathway followed during hydrothermal treatment. From the discussion in the results section, it became evident that targeting a reduction in O/C and N/C and an increase in H/C will lead to bio-oils with HHV. Two-Stage hydrothermal treatment with acid-catalyzed HTL (acetic acid) in the second stage at 300°C achieved this target. The elemental and compound characterization results of the biocrude-oils along with detailed mechanistic

explanations substantiate this claim. Specifically, the mechanistic steps that led to this result was a series of decarboxylation and denitrogenation reactions as shown in the discussion section. Reaction severity and acidic pH led to a decarboxylation reaction by the removal of CO₂ into the gas phase and a denitrogenation reaction by the cleavage of the amino group in the form of NH₃ into the aqueous phase. Performing HTL under acid-catalyzed conditions in this study avoided the formation of nitrogen-heterocyclics by limiting the Maillard reaction as supported by previous studies.

While we see an improvement in the Two-Stage hydrothermal treatment under acidic conditions with the addition of acetic acid, the continuous addition of the acid is not sustainable or practical when looking at a continuous large-scale process. Acetic acid was chosen in this study because of its reliability as a recoverable organic acid from the aqueous phase. It can be seen as a reusable catalyst by looking at a previous literature study on using wet oxidation methodology to convert all organic acids to acetic acid in the aqueous phase. Among all the major organic acids detected in the aqueous solution from the HTL process, acetic acid is the one that is significant in concentration and stable at higher thermochemical conditions compared to formic, lactic, or other organic acids, etc. Hence, acetic acid as a potentially sustainable green catalyst with chemical stability and recyclability through the organic recovery of the aqueous phase solutions from the hydrothermal treatment. Thermochemical processing of the aqueous phase provides an opportunity to recover organics in the form of acetic acid and nutrients in the form of fertilizer (struvite) or ammonia to get us closer to a circular bioeconomy by utilizing all the products of the hydrothermal processes.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

We have shown how commercial waste management treatment methods like landfilling, incineration, and anaerobic digestion do not completely address challenges and opportunities for sustainably managing wet biomass wastes and dilute organic waste streams. In this experimental study, Hydrothermal Carbonization (HTC) and Hydrothermal Liquefaction (HTL) have been shown to provide promising alternatives for wet wastes that add value by improving conversion and the quality of products produced. This study adds to much of the previous literature on the valorization of biomass including agricultural wastes like manure, food waste, sewage sludge, algae, etc. What makes this study unique is its identification of optimized conditions in a two-stage process for maximum energy recovery of biocrude-oil and maximum nutrient recovery in the aqueous phase. Coupling this with the evaluation of the reaction pathway enabled the development of a plausible reaction mechanism to describe the formation of the compounds formed in the bio-oil. By performing an array of experiments at base-case conditions and at the two-stage conditions, we were able to obtain a deeper understanding of what controls the characteristics of bio-oil produced from processing chicken manure by direct HTL and by two-stage (HTC-HTL)

In the study of the two-stage process, we found that a reaction temperature of 190°C for 30 minutes were optimal for stage-1 HTC of chicken manure to produce hydrochar with 54% mass yield, 56% carbon recovery, and 36% nitrogen recovery. Second-stage HTL with the addition of 0.2 M acetic acid (AA) at 300°C and 30 minutes was ideal for bio-oil with a maximum HHV (37 MJ/kg) and maximum mass yield (11 wt% w.r.t chicken

manure). On the other hand, single stage, base-case HTL processing of chicken manure resulted in bio-oil with a HHV of 32 MJ/kg and a mass yield of 18 wt%. Targeting for maximum mass yield (quantitative) and HHV (qualitative) in this study highlights the improvement in the bio-oil quality to be used as a drop-in fuel with the two-stage process.

While this study provided optimized conditions w.r.t energy recovery for the two-Stage process, the ideal process conditions were chosen from pre-defined range of experimental parameters. An improvement to the model could be achieved by using digital tools to optimize the parameters and identify the specific reaction conditions needed to produce the best characteristics of the bio-oil.

This study of utilizing a two-stage hydrothermal treatment process provides a starting point for maximizing energy and nutrient recovery through agricultural wastes valorization to produce bio-oils with better HHV and for recovering N and P nutrients to the aqueous solution. Ultimately we believe that dual optimization of hydrothermal treatment will be needed to approach a circular bioeconomy as depicted in Fig. 34, where agricultural wastes are valorized into renewable energy and nutrient products for Energy-rich and nutrient-rich products are formed that can be recirculated back and reuse, in the agricultural industry sector. This approach will help to make the food industry more self-reliant and with lower-carbon emissions compared to conventional food production methods that rely heavily on fossil-fuel-based inputs for energy and nutrients, in addition, diverting food waste streams from landfills will lead to a significant decrease in overall fugitive methane emissions and reduced nitrogen and phosphorous induced eutrophication from runoff into river basins and lakes.

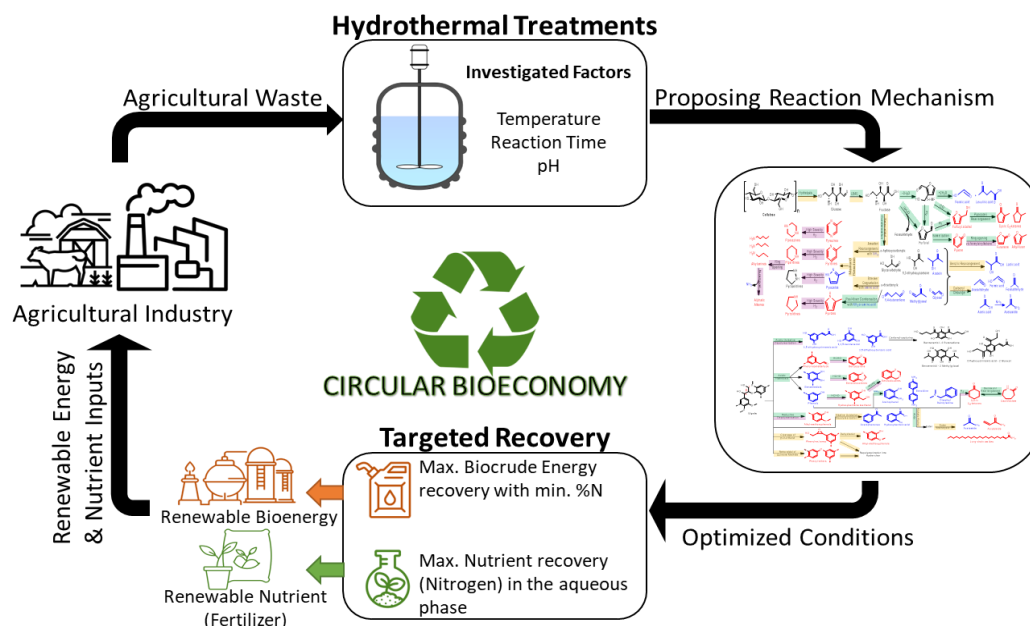


Figure 34 Flowchart Outline on Circular Bioeconomy

While acetic acid was shown to be recoverable from the aqueous phase in previous study (Silva Thomsen et al., 2022), it was still limited to sewage sludge as a feedstock. A future study could focus on agricultural wastes like dairy or chicken manure and look at wet oxidation/filtration processing methods on the aqueous solution from HTL/HTC of manure to maximize the conversion of organics to acetic acid. Doing a detailed experimental compound characterization on the Process Water (PW)/Aqueous Phase of such hydrothermal treatment systems can support the proposed future study. To summarize, this study provides a first account of the characteristics of the bio-oil from two-stage hydrothermal treatment of chicken manure along with an understanding of the reaction mechanism through compound characterization of the bio-oil.

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APPENDIX

Table 13 Elemental Composition of Hydrochar and Bio-Oil in Base-Case (wt%)

Solid & Oil	250°C			300°C			350°C		
C% HC	32.10	29.46	29.13	24.52	26.56	25.69	22.92	22.64	20.45
C% DWO	53.43	58.23	61.79	59.64	55.02	63.53	53.16	61.13	63.37
C% EWO	53.22	57.37	57.93	56.25	57.83	57.93	59.01	60.85	60.44
C% DSO	70.41	70.36	72.38	71.11	71.21	72.54	71.12	71.51	74.40
H% HC	3.16	2.50	2.38	2.31	2.32	2.02	1.90	1.99	1.54
H% DWO	6.00	6.06	6.62	6.27	5.80	6.88	5.99	6.61	6.80
H% EWO	5.65	5.68	5.81	5.76	5.54	5.86	6.23	5.84	5.81
H% DSO	8.99	8.26	8.69	7.43	7.86	8.09	8.35	7.90	8.18
N% HC	3.28	2.84	2.65	2.06	2.49	2.10	1.78	3.50	1.51
N% DWO	11.12	12.68	13.66	8.86	8.85	9.28	6.40	8.33	7.47
N% EWO	11.98	13.92	15.08	9.65	10.89	9.57	8.14	9.80	8.08
N% DSO	4.19	4.21	4.12	4.45	5.19	4.67	4.45	5.28	4.26
R% HC	61.45	66.11	65.85	71.10	68.62	70.19	73.40	71.87	76.50
R% DWO	29.46	23.03	17.93	25.22	30.33	20.32	34.45	23.92	22.37
R% EWO	29.14	23.03	21.17	28.33	25.75	20.32	26.62	23.51	25.68
R% DSO	16.41	17.17	14.81	20.04	15.74	14.71	16.08	16.27	13.17

*(%O=%R-%Ash)

Table 14 TOC & TN of Aqueous Phase from Base-Case

Liquid	250°C			300°C			350°C		
TOC (mg/L)	12783.91	12661.62	12106.27	8070.10	8736.08	8482.93	7499.58	8151.00	7805.89
TN (mg/L)	2497.11	2439.01	2326.77	1967.09	2197.09	2467.74	2295.31	2444.00	2541.89

Table 15 Elemental Composition of Hydrochar in Stage-I (wt%)

Hydrochar	160°C30min		160°C60min		190°C30min			190°C60min		220°C30min		220°C60min		250°C30min		250°C60min	
C%	35.69	37.98	34.51	33.73	40.48	38.34	38.46	40.04	37.45	39.08	39.57	39.14	39.17	38.06	39.28	39.28	39.99
H%	4.27	4.64	4.49	5.19	4.51	4.69	4.52	4.90	4.38	4.19	4.15	4.47	4.40	3.89	4.05	3.75	3.83
N%	3.21	3.53	3.03	2.98	2.84	2.86	3.01	2.62	2.49	2.79	2.79	2.85	2.77	3.02	3.16	3.05	3.08

Table 16 TOC & TN of Aqueous Phase from Stage-I

Liquid	160°C30min		160°C60min		190°C30min			190°C60min		220°C30min		220°C60min		250°C30min		250°C60min	
TOC (mg/L)	17575.9	16506.1	16317	16466.4	15147	13460.2	13918.6	12614	12286	13315	13426.4	13493.6	13968.8	12878.9	13267	11508	11733.7
TN (mg/L)	2363.7	2132.32	2120.03	2095.8	2766.9	2166.41	2170.15	2203.8	2349.6	2551.5	2622.67	2634.61	2653.64	2448.53	2497.4	2389.33	2396.51

Table 17 Elemental Composition of Hydrochar and Bio-Oil from Stage-2 (wt%)

Solid & Oil	300°C	300°C 0.2M AA	350°C	350°C 0.2M AA
C% HC	29.13	28.97	26.64	25.47
C% DWO	61.54	57.99	62.22	59.56
C% EWO	62.55	53.23	63.34	53.30
C% DSO	73.71	72.84	75.34	73.62
H% HC	2.48	2.38	1.96	1.66
H% DWO	7.09	7.10	7.37	7.16
H% EWO	7.37	6.48	7.04	6.20
H% DSO	9.62	9.94	10.30	10.24
N% HC	2.33	2.37	1.87	1.93
N% DWO	8.07	6.21	7.18	5.28
N% EWO	8.14	4.57	7.14	4.38
N% DSO	3.88	2.94	3.07	2.46
R% HC	66.05	66.29	69.53	70.94
R% DWO	23.15	28.70	23.24	28.00
R% EWO	22.23	35.71	22.49	36.13
R% DSO	12.78	14.28	11.30	13.68

Table 18 Compound Characterization of Bio-Oils from Base-Case (Area%)

Bio-Oil Compound Characterization	250°C	300°C	350°C
O-Heterocyclics	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
N-Heterocyclics	3.50 ± 0.74	4.84 ± 0.56	6.51 ± 1.66
Amides/Amines	2.61 ± 1.16	9.90 ± 1.08	4.33 ± 2.13
Nitriles	0.00 ± 0.00	0.09 ± 0.09	0.18 ± 0.07
Carboxylic Acids & Ester	80.43 ± 5.16	43.24 ± 7.17	50.57 ± 5.06
Alcohols (Phenols)	2.92 ± 0.43	9.56 ± 1.00	6.79 ± 1.11
Ketones	0.38 ± 0.13	5.15 ± 3.09	5.58 ± 3.29
Aliphatic HC	0.05 ± 0.04	2.77 ± 0.13	3.15 ± 0.11
Ether	0.08 ± 0.08	0.00 ± 0.00	0.00 ± 0.00
Aldehydes	0.00 ± 0.00	0.00 ± 0.00	1.29 ± 1.29
Total	88.04 ± 5.36	75.46 ± 7.97	76.92 ± 6.82

Table 19 Compound Characterization of Bio-Oils from Two-Stage (Area%)

Bio-Oil Compound Characterization	Two-Stage							
	300°C		300°C 0.2M AA		350°C		350°C 0.2M AA	
O-Heterocyclics	0.00	± 0.00	0.00	± 0.00	0.51	± 0.00	0.00	± 0.00
N-Heterocyclics	4.50	± 0.02	1.34	± 0.19	1.87	± 0.00	1.52	± 0.19
Amides/Amines	8.35	± 1.90	2.87	± 0.08	7.95	± 0.00	3.29	± 0.03
Nitriles	0.18	± 0.10	0.07	± 0.07	0.22	± 0.00	0.18	± 0.05
Carboxylic Acids & Ester	41.41	± 3.33	48.63	± 0.11	38.23	± 0.00	41.75	± 5.40
Alcohols (Phenols)	8.49	± 0.11	8.03	± 2.13	6.58	± 0.00	11.88	± 2.88
Ketones	2.45	± 0.03	1.54	± 0.54	6.24	± 0.00	4.09	± 1.13
Aliphatic HC	4.84	± 0.62	3.79	± 0.57	8.39	± 0.00	8.47	± 4.33
Ether	0.07	± 0.03	0.00	± 0.00	0.24	± 0.00	0.00	± 0.00
Aldehydes	0.12	± 0.07	0.00	± 0.00	0.11	± 0.00	0.08	± 0.03
Total	70.23	± 3.88	66.24	± 2.28	70.34	± 0.00	71.21	± 7.59

Table 20 Compound Characterization of Aqueous Phase from Base-Case and Second Stage

Aq. Phase Compound Characterization (mg/L)	Base-Case		Two-Stage			
	300°C	350°C	300°C	300°C 0.2M AA	350°C	350°C 0.2M AA
Lactic Acid	0.00	0.00	0.00	29088.28	6916.29	20318.26
Formic Acid	16106.43	10786.88	8721.28	0.00	0.00	0.00
Acetic Acid	12523.04	12086.45	6793.95	24690.67	5900.04	29954.30
1,3 cyclopentanedione	8480.61	4104.51	4414.44	4603.10	2211.60	3047.80
2(5H) Furanone	0.00	0.00	0.00	0.00	0.00	23.80
2-Cyclopenten-1-one	37.88	0.00	38.70	86.01	35.31	80.67
3-Methyl-1,2-cyclopentanedione	0.00	0.00	0.00	0.00	0.00	0.00
Catechol	21.01	0.00	0.00	105.14	0.00	101.18
Furfural	0.00	0.00	0.00	0.00	0.00	0.00
Pyrazine, methyl-	275.33	171.39	99.74	76.63	80.11	100.16
2-cyclopenten-1-one, 2-methyl-	97.34	74.86	118.59	97.15	127.61	140.09
5-Methylfurfural	0.00	0.00	0.00	0.00	0.00	0.00
Phenol	110.30	90.69	111.87	69.68	86.55	111.72
2-Methoxyphenol (guaiacol)	78.35	0.00	41.40	61.90	31.92	39.84
2,6 Dimethoxyphenol	27.54	17.08	0.00	0.00	0.00	17.70
p-cresol	10.77	19.27	11.10	19.15	18.99	48.54
2-Methoxy-4-methylphenol	15.74	16.01	10.64	11.78	13.79	0.00
4-ethyl-2-methoxyphenol	8.13	0.00	0.00	0.00	0.00	0.00