Hydrothermal Liquefaction of Municipal Sludge and Biocrude Upgrading Using Carinata Oil

by

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Abstract

Crude oil is a finite resource. Due to an advancement in technology, it is now possible to produce petroleum from very tight and hard reservoir formations. However, the global outcry towards the adoption of sustainable and renewable energy sources has led to research into feedstocks that could justify the investment. This will expectedly limit the role of crude oil in the global economy, and will favor the use of wet wastes such as municipal sludge.

Municipal sludge is a product of waste treatment processes. Conventional sludge treatment methods include incineration, land application and composting. The release of toxic substances into the atmosphere coupled with demonstrated leaching of contaminants into the subsurface are making these treatment methods unpopular. There is, therefore, a need to carry out research into better ways of valorizing this waste resource. This study presents the comparison on the effect of temperature and solids content on the product yield and fuel quality of municipal sludge hydrothermal liquefaction (HTL) products with and without using red clay as a catalyst. HTL was carried out on three sample types namely: Pre-dried sludge (PD: dewatered secondary sludge that was further pre-dried prior to use), Secondary sludge (Sec: after aerobic digestion but before running through the belt press) and Thickened sludge (TK: secondary sludge that has gone through the mechanical press for solids content increase at the treatment station).

HTL was carried out at 300ºC and 325ºC, with a reaction residence time of 1hour and a continuous stirring speed of 95RPM maintained in all experiments. The highest oil yield of 37.7±1.6 wt.% (dry basis, ash free) was obtained in the thickened sludge liquefied at 325ºC, while the highest char yield of 20.6±1.6 wt.% was obtained in the catalyzed secondary sludge liquefaction at 325ºC.The higher heating value of the produced biocrudes ranged from 24.2±0.3

MJ/kg (catalyzed secondary sludge oil produced at 300ºC) to 35.0±0.8 MJ/kg (pre-dried sludge oil produced at 300ºC). The total acid number (TAN) was lowest (13.1±0.3 mg KOH/g) for the thickened sludge biocrude produced at 300ºC, and was highest (19.8±1.6 mg KOH/g) for the secondary biocrude produced at 325ºC. The integration of the red clay catalyst significantly improved the TAN value of all produced biocrudes (Pre-dried sludge biocrude: 19.3±0.4 to 17.4±0.1 mg KOH/g at 300°C and 15.7±0.8 to 13.8±0.3 mg KOH/g at 325°C; Secondary sludge biocrude: 17.0±0.2 to 14.9±0.1 mg KOH/g at 300°C and 19.8±1.6 to 17.9±0.3 mg KOH/g at 325°C; Thickened sludge biocrude: 18.6±0.4 to 15.7±0.2 mg KOH/g at 325°C). The obtained char products had a low HHV due to high oxygen content. The produced aqueous phase was rich in nutrients with high concentration of ammonium ions observed.

Catalytic upgrading of municipal sludge based biocrudes became necessary due to high amount of heteroatoms (N,S and O) present in the oil. The cost of catalysts could significantly impact the economics of the overall cost of the fuels, and research into low cost catalytic options has become necessary. The synergistic effect of hydrotreating this cracked oil with municipal biocrude over inexpensive Ni/SiO_2-Al_2O_3 is explored in this study. Triglycerides such as waste cooking oil and non-edible oils have been studied for possible reintegration as liquid transportation fuels. Esterification processes have revealed that the produced biodiesel was much comparable with petroleum-based diesel, thereby making the co-processing of both fuels very effective. Catalytic cracking of these triglycerides helps to break the glyceride backbones, thereby producing fuels with improved viscosity and higher heating value.

The catalytic upgraded oil yields at 250°C 3h, 300°C 1h, 350°C 1h and 350°C 30min did not vary significantly in terms of the liquid product yield; although longer processing times favored the production of more solids. The higher heating value of the produced liquids was also

comparable to petroleum-based liquid fuels, with the highest value recorded being 45.1±0.6 MJ/kg from processing at 350ºC for an hour. The 350°C 30min processing condition was most efficient, and was studied further. The increase in the catalyst loading rate resulted in the production of liquid fractions with lower viscosity and acidity, and the production of higher carbon gases due to further cracking of heavier compounds. The use of uncracked oil as opposed to cracking resulted in significantly lower liquid yield with lesser hydrogen consumption, suggesting slower levels of hydrodeoxygenation. The liquid, however, had a significantly lower total acid number of 0.89±0.07 mg KOH/g.

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Chapter 1

Introduction

1.1 Importance of the bioeconomy

The bioeconomy refers to a localized economy in which every nation depends solely on resources that have been made readily available by nature to supply her energy and chemical demands, as opposed to the current global dependence on fossil fuels. For this concept to thrive however, each country needs to develop policies that replace products derived from fossil fuels with products from renewable biological alternatives. An example of this type of policy is the Energy Independence and Security Act of 2007 in the United States, which mandates a Renewable Fuel Standard (RFS) of 36 billion gallons of annual biofuel production by 2022 [1]. The current levels in 2020 stand at 20.09 billion gallons fuels from renewable sources with 15billion gallons from conventional biofuels and 5.09 billion gallons from advanced biofuels [2]. There is therefore a lot of spare capacity not being met currently, providing a unique opportunity for sludge-based biofuels to contribute towards meeting the quota.

This thesis therefore demonstrates a feasible pathway to produce drop-in fuels from sewage sludge sources.

1.2 Municipal sewage sludge as a viable feedstock

Sewage sludges are heterogeneous mixtures obtained from waste treatment processes. Depending on the treatment process, sewage sludge contain varying quantities of protein (15 – 41%), lipids (5 – 35%) and cellulose (8 – 15%) [3]. According to the 2016 Billion-Ton Report of energy resources in the United States, municipal solid wastes (MSWs), a viable co-composting feedstock was identified as the most available resource at $60 per dry ton and with the guarantee of 155 million dry tons annually by 2040 [4] .The direct use of sewage sludge for land application could lead to fatal infections due to increased risk of human exposure to parasites such as Ascaris and Trichuris [5]. Other traditional sludge management methods such as incineration and co-composting can result in the emission of toxic substances into the atmosphere [6]. Since the cost of sludge disposal is about 45 – 60% of overall treatment costs of wastewater treatment facilities [7], development of alternative sludge treatment methods that could recover part of these costs by converting treatment wastes to energy, chemicals and products can be attractive to these plants.

1.3 Hydrothermal conversion of wet feedstocks

Hydrothermal liquefaction (HTL) is a thermochemical conversion process that utilizes the ionic properties of water at sub and supercritical conditions of temperature and pressure to valorize wet biomass feedstocks such as sewage sludge to carbon-rich biocrude [8]. The HTL process starts with a rapid depolymerization stage followed by organic decomposition and recombination that lead to generation of biocrude with similar properties to algal HTL crudes [9]. The integration of catalysts in HTL reactions represents a substantial percentage of the overall project cost, due to its role in reducing the activation energy and improving product quality [10,11]. The biocrude derived from the liquefaction of sludge biomass can be used as-is for bunker (heavy) fuel purposes but will require further upgrading to meet liquid transportation fuel standards [12].

1.4 Hydro-processing of biocrude to hydrocarbon fuels

Hydro-processing uses hydrogen to remove heteroatoms such as oxygen, nitrogen and sulfur from biocrudes. Upgrading biocrude in the presence of hydrogen can be categorized into hydrogenation, hydrocracking, deoxygenation, and denitrogenation, depending on the prevalent reaction chemistries. Silica and alumina-supported catalysts have gained widespread adoption in industrial cracking operations, due to their adjustable acid strength and stability at high temperatures [13]. Nickel-based catalysts belong to the group of transition metal catalysts, and are preferred over noble metal catalysts due to their cheaper cost and their ability to control radical polymerization [14]. Nickel, when impregnated on a silica-alumina support, has been found to be versatile both in vegetable oil and phenolics in the conversion of oxygen species in organic compounds into hydrocarbons [15,16]. Despite the efficacy of the nickel on silica-alumina heterogeneous catalyst in acting as a hydrotreating catalyst, catalyst deactivation as a result of coke formation is still a challenge.

1.5 Challenges of hydrothermal processing and biocrude upgrading

Continuous and batch hydrothermal processing of sewage sludge feedstock has been largely successful, primarily due to its lower operating temperature and the ability to process wet materials. To ensure the competitiveness and strong business case of this technology however, some challenges need to be addressed. Current challenges of hydrothermal processing and upgrading of sewage sludge include:

- The biocrude obtained from HTL of sewage sludge generally have high viscosity (611-818 cp), as a result of the polymerization of reactive oxygenated functional groups such as C=O bonds [17]. This is a concern if the biocrude must be transported over long distances to processing facilities.
- Relatively high sulfur content of the HTL derived biocrude (1-3%) from sewage sludge may cause severe corrosion challenges due to the formation of acids [18].
- While total oxygen removal has been achieved during the hydrotreating of sludge based biocrudes, the total removal of nitrogen still presents a significant challenge [19]. There is,

therefore, more need for research into custom-designed catalysts that can help achieve total de-nitrogenation.

1.6 Research objectives

Sludge dewatering, liquefaction, aqueous phase treatment, transportation and hydrotreating costs represent some of the most important considerations that can affect the minimum fuel selling price of sludge derived hydrocarbon fuels [20]. A very sizeable of project cost is the cost of catalyst, which can be as high as $1.3 million per annum for a 110 dry ton/day sludge HTL plant [21]. Numerous studies on the hydrothermal liquefaction of sewage sludge have addressed the effects of homogenous and heterogeneous catalysts, operating conditions of temperature and pressure, residence time, solvents and co-solvents; and initial pretreatment processes on the yield and properties of obtained biocrude. This research addresses the challenges summarized in the last section regarding the hydrothermal liquefaction of sewage sludge by investigating the impacts of 2 catalysts: cheap red clay and heterogenous Ni/SiO_2-Al_2O_3 for hydrothermal liquefaction of sewage sludge and upgrading of the produced biocrude respectively. The specific objectives of this study were as follows:

1.6.1 Catalytic liquefaction of municipal sludge

In this study, HTL of three sludge samples was carried out and assessed for the effect of temperature (300ºC and 325ºC) and solids content (5%, 15% and 20%) on the yields and properties of derived products. The effect of using red clay as a catalyst was also studied. The three sludge samples were secondary sludge (5% solids content), thickened sludge (15% solids content) and pre-dried sludge (dried sludge maintained at 20% solids loading for liquefaction). The pre-dried sludge also served as a base case for comparison with the other sludge classes which were converted as received from the municipality. The biocrude and other by-products (gas, biochar and aqueous product) obtained from all experiments were analyzed for their physical and chemical properties. The details of the experiments, results and conclusions are summarized in Chapter 3.

1.6.2 Municipal sludge co-upgrading over Ni/SiO_2-Al_2O_3 catalyst

In this study, the HTL biocrude obtained from the hydrothermal liquefaction of sewage sludge at 325°C was co-upgraded with cracked hexane-extracted *Brassica Carinata* oil (HEBCO) using the heterogeneous Ni/SiO_2-Al_2O_3 as catalyst. Upgrading of only biocrude with catalyst led to rapid polymerization and solidification of the biocrude even before reaching set temperature. There was therefore, a need for a solvent based approach to assist in the upgrading process. The effect of process parameters such as temperature, time and catalyst loading on upgraded oil yield and quality was assessed. The details of this novel approach to upgrading biocrudes with high heteroatom content is presented in Chapter 4.

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Chapter 2

Literature review

2.1 Energy framework

Energy is fundamental to the progress of the society both now and in the coming generations. The 2019 International Energy Outlook documented that the world energy consumption increased by nearly 50% from 2015 to 2018, and forecasted this figure to approach an astronomical value of 911 quadrillion British thermal units (Btu) by 2050 [1]. Most of this consumption has been determined to result from non-OECD countries, due to the anticipated annual growth in their gross domestic product to 3.8% as compared to 1.5% for OECD countries. This can be attributed to increased consumption by expanding industrial sector, which results in renewable energy becoming the leading source of primary energy by the year 2050. Although fossil fuels will continue to meet most of the world’s energy demand, the global oil trades volume is expected to reduce from a 2018 level of 80% to 75% by 2040.

As a result of breakthroughs in unconventional resources due to hydraulic fracturing, the United States became a net energy exporter in 2020 [2]. The import of natural gas from Western Canada has been noticed to continue a steady decline from historical levels, consequentially leading to increased export of gas to Eastern Canada due to proximity to natural gas plays and recent pipeline infrastructure. The energy consumption in the United States has also increased from 97.8 quadrillion Btu in 2017 to 100.2 quadrillion Btu in 2019, with major increments noticed in natural gas and solar energy consumptions. The surge in solar energy consumption can be attributed to new policies implemented in some states such as California, New Jersey, and Massachusetts to increase electricity generation from renewable sources. This trend is expected to grow, as the combined generation required to comply with state-level renewable portfolio standards (RPS) across the United States has been pegged at 704 billion kilowatt-hours by 2050.

The 2019 BP statistical review of world energy currently estimates the reserves to production ratio (R/P) of oil and natural gas at 50 years and 51 years, respectively [3]. This means that without a significant improvement in technological advancements to improve reserves, the current oil and natural gas reserves can only sustain the world till 2069 and 2070, respectively. Consequently, biofuels production experienced the highest growth in a decade by averaging 9.7% in 2018 with Brazil and Indonesia accounting for almost two thirds of global increase. This presents a strong case for the integration of biomass derived fuels in more sectors of the emerging bioeconomy.

The 2016 Billion-Ton Report on domestic resources integration reveal a potential for increase in biomass production with minimal environmental impacts [4]. Municipal solid wastes (MSWs) were determined to be the largest resource fraction at $60 per dry ton, resulting in an aggregate 2040 total of 155 million dry tons and an additional landfill gas volume of 229 billion ft^3 [5]. Following the economic recession of 2007-2010, the Energy Independence and Security Act (EISA) of 2007 was enacted to prevent adverse effects from low energy prices and to promote domestic biofuel utilization. Figure 2.1 shows the original mandates by biofuel category, requiring a total of 36 billion gallons of renewable fuels in 2022 while capping conventional biofuel (corn ethanol) at 15 billion.

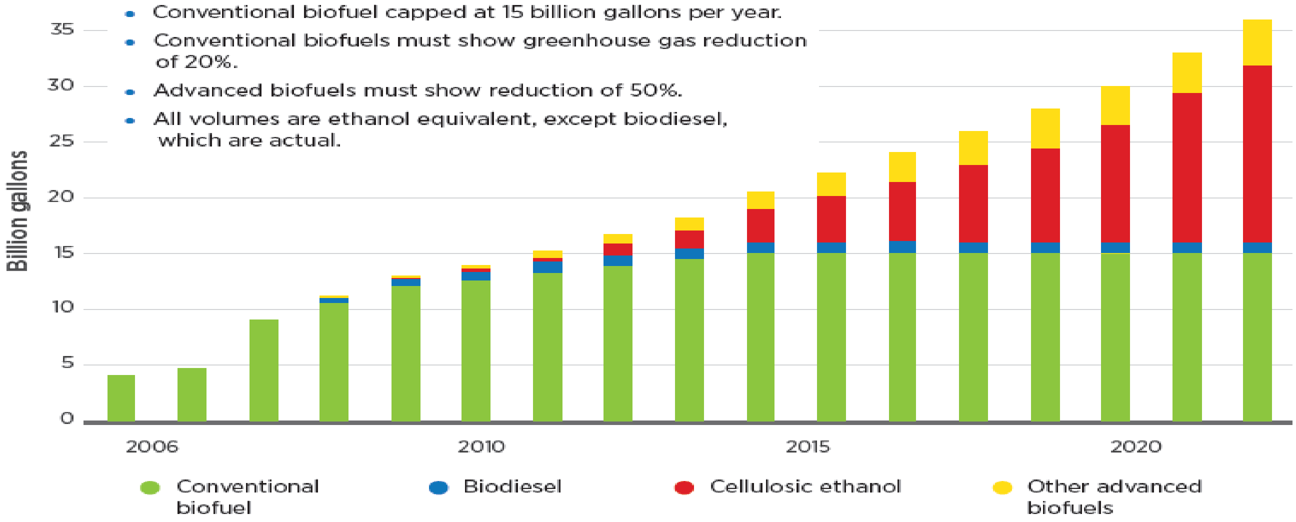

Figure 2.1 RFS Original Mandates by Biofuel Category. Copied from ref. [5] for illustration

For the RFS policy to succeed however, there must be more consumption of biofuels. This has resulted in the blending of ethanol with conventional petroleum-based oil in ratios such as E10, E15 and E85. This represents significant environmental impact, as this ensures that there are reduced emissions from the transportation sector, which accounts for about 28% of US energy consumption [6].

Sulfur content in crude oil barrels is becoming an increasingly discussed topic, as the world shifts to cleaner and better sources of fuel. Nations are favoring sweeter and lighter crudes, and refineries are tweaking their facilities to accommodate more of these preferred feedstocks. Historical data shows that current US crude continues to have decreasing sulfur content, with a level of 1.33 percent recorded as at July 2019 [7].

2.2 Biomass and biofuels

Biomass can be defined as any organic (i.e. decomposing) material derived from plants or animals, which are available on a renewable basis. These includes wood and agricultural crops, herbaceous and wood energy crops, municipal organic wastes as well as manure [8]. Biomass is widely considered to be a clean source of energy because the released carbon dioxide (CO_2) during combustion is recaptured by the growth of the same material. Biomass can be largely classified into agricultural residues, dedicated energy crops, forestry by-products, industrial residues (wood industry residues, food industry residues and industrial products e.g. pellets and briquettes from sawdust and shavings) and waste [9]. Based on constituents, biomass can be largely classified into carbohydrates, lignin, and fats/oils [10]. Biomass is among the most promising feedstock for the generation of liquid transportation fuels, having the potential for supplying up to 35% of energy needs in both industrialized and developing countries [11].

Agricultural crops represent the largest source of cellulose worldwide, with an estimated annual production of 2×10^{11} tons of cellulosics [12]. This is considered the most abundant waste after harvesting, hence providing an opportunity for utilization in order to solve disposal issues and subsequently reduce treatment costs [13]. The current major use of biomass as a resource is for heat generation purposes at individual, central and district heating systems due to the higher heating value and favorable combustion properties [14]. Moreover, there is an identified possibility of achieving greater energy efficiency and material recycling on switching to cleaner energy technologies in food and fiber processing industries [15,16].

Biofuels are fuels that derive their energy as a result of a biological carbon fixation process; encompassing solid biomass, liquid fuels, biogas, and fuels derived from biomass conversion processes [17]. A distinguishing factor between fossil fuels, which also accumulated from ancient fixation of organic matter, is the presence of carbon materials which belong to a different geologic age. The International Energy Agency estimates that biofuels have the potential to meet more than 25% of the world’s demand for transportation fuels by 2050. This is because of some preferential advantages which include renewability, reduced emission of greenhouse emissions, reduction in pollution levels and economic security [18]. Proven and currently prospected sources of biofuels include algae, carbohydrate rich biomaterials (sugars), oil rich biomaterials and agricultural wastes (organic and inorganic).

Biofuels have been available since the development of the diesel engine by Rudolf Diesel, as it was designed to run on a variety of feedstocks including vegetable oils [19]. Henry Ford further promulgated this concept in his design of the Ford Model T, which could run on gasoline, kerosene, and ethanol [20]. The discovery and abundant supply of fossil fuels at the time however ensured that the use of biofuels in those systems would not see the light of the day. The 20th century World War II oil shortage and the oil crisis of 1970s presented opportunities for the use of biofuels, and that has been the norm until recently. Modern classification of biofuels considers the existence of four generations of biomass derived fuels.

First generation biofuels are fuels of sugar, starch, vegetable oil or animal fats origin which have been exploited for nearly three decades [21]. The major conversion process for these fuels includes enzymatic fermentation or transesterification processes which lead to the production of fuels such as biodiesel, ethanol and methanol fuels [22]. Production of fuels through this route has however come under serious scrutiny due to issues such as the water and energy requirements, by-products disposal, large capital costs and the never ending “food versus fuel” debate [23-27]. There was therefore a need for another category of fuels with lesser demands on resources, coupled with minimal environmental impacts.

Second generation biofuels were developed to address some of the challenges of the earlier generation, by incorporating residual biomass in the production mix and subsequently lead to more sustainable processes. Feedstocks in this category include lignocellulosic biomass, municipal wastes and inedible oils/greases. Technologies used for converting these fuels include pyrolysis, gasification in tandem with Fischer-Tropsch synthesis and the relatively newer hydrothermal liquefaction process [28]. The use of these feedstocks has been found not to directly affect human consumption, but challenges such as pre-treatment costs and larger land requirements are the delaying the scale-up to commercial production [29].

Third generation biofuels refer to fuels that are produced by making use of non-arable land, thus relieving the pressure on land use [30,31]. This category consists of feedstocks generally referred to as Aquatic Microbial Oxygenic Photoautotroph (AMOP), and includes cyanobacteria, algae, and diatoms [32]. Algae appears to be the only feedstock in this category capable of meeting global demand for transport fuels and address current global warming challenges, provided water and pretreating issues can be efficiently addressed [33-36].

Fourth generation biofuels are the most recent classification, comprising of feedstocks requiring non-arable land and do not require the destruction of the biomass prior to conversion processes. Photobiological solar fuels and electrofuels are candidates in this category that are currently being researched, as their high capital costs and long processing times are major stumbling blocks [37].

2.3 Sewage sludge as a resource

Sludge or raw sludge is any residual produced during primary, secondary, or tertiary wastewater treatment processes which has not undergone any pathogenic reduction process [38]. The world population is increasing dynamically, subsequently increasing demand for precious resources such as water. Thus, available water bodies such as wastewater must be assessed and treated in order to meet this need [39]. Prior to public discharge however, there is a need to effectively treat wastewater bodies in order to ensure adherence to pollutant and pathogen levels set by protection agencies. The overall aim, however, remains to remove suspended solids, eliminate biochemical oxygen demands (BODs), pathogens and nutrients [40]. Sludge can therefore be considered as heterogenous mixtures of organic compounds, micro-organisms and heavy compounds. The presence of organics such as nitrogen and phosphorus, and inorganics such as aluminates present an opportunity for the recycling and reuse of important resource [41-45]. Table 2.1 presents the typical composition and properties of different sludge classes.

Table 2.1 Typical chemical composition and properties of different sludge types [46]

Item/sludge	Untreated primary		Digested primary		Activated range
	Range	Typical	Range	Typical	
Total dry solids (TS), %	2.0-8.0	5.0	6.0-12.0	10.0	0.83-1.16
Volatile solids (% of TS)	60-80	65	30-60	40	59-88
Grease and fats (% of TS)					
Ether soluble	6-30	−	5-20	18	−
Ether extract	7-35		−	−	5-12
Protein (% of TS)	20-30	25	15-20	18	32-41
Nitrogen (N, % of TS)	1.5-4	2.5	1.6-6.0	3.0	2.4-5.0
Phosphorus (P_2O_5, % of TS)	0.8-2.8	1.6	1.5-4.0	2.5	2.8-11.0
Potash (K_2O, % of TS)	0-1	0.4	0.0-3.0	1.0	0.5-0.7
Cellulose (% of TS)	8.0-15.0	10.0	8.0-15.0	10.0	−
Iron (not as sulfide)	2.0-4.0	2.5	3.0-8.0	4.0	−
Silica (SiO_2, % of TS)	15.0-20.0	−	10.0-20.0	−	−
Alkalinity (mg/l as $CaCO_3$)	500-1500	600	2500-3500		580-1100
Organic acids (mg/l as Hac)	200-2000	500	100-600	3000	1100-1700
Energy content	10,000-12,500	11,000	4000-6000	200	8000-10,000
pH	5.0-8.0	6.0	6.5-7.5	7.0	6.5-8.0

TS: Total solids; Hac: Acetic acid

From the table above, it can be seen that sewage sludge are neutral, due to a balance in the concentration of organic acids and carbonates present. Wastewater Treatment Plants (WWTPs) are facilities that can adequately process incoming wastewater streams and ensure the compliance of effluents with slated regulatory controls. Plants are often adapted to their respective localities, as waste streams vary based on factors such as community lifestyles and technologies at disposal [47,48]. In these facilities, the removal of BODs, suspended solids, nutrients (in the forms of nitrate nitrogen, nitrite nitrogen, ammonium nitrogen and phosphates), coliform bacteria and the overall reduction in toxicity levels are the major priorities [40]. Figure 2.2 presents a schematic of a waste treatment facility located in Auburn, Alabama USA where sewage sludge samples from this study were obtained. Prior to the main wastewater treatment steps, there exists a pre-treatment stage which involves the removal of large objects and non-degradable materials using bar screens and grit chambers.

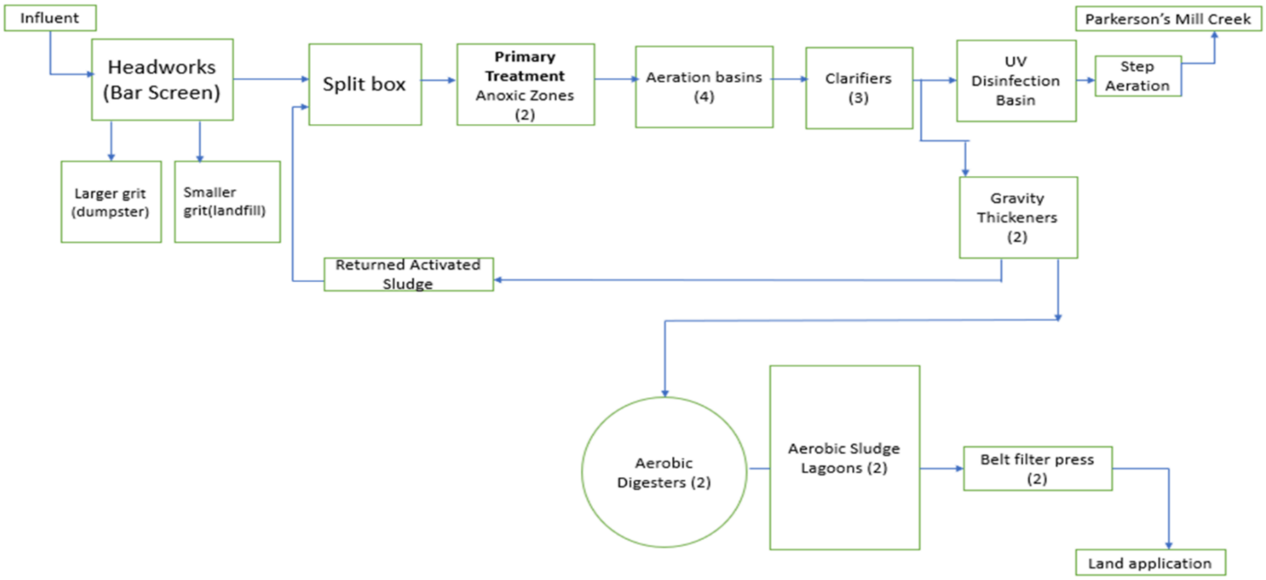

Figure 2.2 Schematic of H.C. Morgan wastewater treatment facility

After the removal of large solids and grits, the primary treatment continues with waste settlement in two primary clarifiers. These are very large tanks in which anoxic conditions are prevalent, whereby suspended solids settling at the bottom of the tank due to gravity effects. These settled materials are termed biosolids, with technically astute tanks being able to remove 40% of BOD through this process [49]. However, the same cannot be said of pathogen removal rates as these tend to vary greatly with respect to different micro-organisms present [50,51]. The sludge from this process is sent to the sludge thickener for concentration prior to disposal, while the liquid phase is sent to a secondary treatment step.

Following the sedimentation treatment in the anoxic zones, wastewater is pumped through trickling filters into aeration basins. This process signals the beginning of secondary treatment processes with the goal of utilizing bacteria and algae to metabolize the organic matter in the wastewater. The overall objective of suspended solids and BOD reduction is therefore met in these secondary treatment step, using either fixed film or suspended growth media [52,53]. Following the end of the treatment process, the microorganisms settle to the bottom of the bioreactor where they are retrieved and subsequently recycled during other treatment activities. The effluent water is sent through ultraviolet filters for further treatment prior to discharge into open waters, while the obtained solids undergo further treatment processes prior to final use. These treatment processes include: primary sedimentation tanks (for further solids and BOD removal), gravity thickening (for solids concentration), aerobic digestion (for more organic matter and volume reduction), aerobic sludge lagoons (for sludge holding and treating) and belt-pressing (for sludge thickening).

Tertiary treatment, such as ultraviolet disinfection, refers to the chemical or biological removal of inorganic ions in wastewater, prior to discharge into groundwater bodies. A tertiary treatment is deemed complete if it is successfully able to remove ammonium, nitrates, and phosphates from wastewater. However, this could easily increase the overall cost about four times beyond the primary treatment [54]. Industrial and agricultural wastewater discharged after treatment have been found to contain nitrogen and phosphorus concentrations up to three times the level found in natural open waters, thus necessitating the need for disinfection [55].Advanced wastewater techniques exist, and they are based on processes such as ozonation, chemical precipitation, carbon adsorption or reverse osmosis.

2.4 The challenge of sewage sludge management

Sewage sludge is the major waste stream generated at the wastewater facilities, albeit its management is difficult and has high cost implications [56]. The sludge output from different countries also seems to be annually increasing, with more than 10 million tons of dry sludge being produced in EU, and China also recording well over 20.76 million tons of 80% moisture sludge [57-59]. Because of this, most of the generated sludge (70%) find its way to landfills as only a fraction is used for agricultural purposes [60]. Land application of sludge has been a topic of debate recently, owing to odor issues and possibility of metal and pharmaceutical contamination [61,62]. Land application is most suited to small wastewater systems that process waste streams less than the equivalent from 20,000 people [63]. Landfilling of sewage sludge has been heavily discouraged, due to the increased risk of ammonia production and leaching effects coupled with the rising cost of landfill facilities, thus providing opportunities for sustainable approaches to sludge management [64]. Incineration is also a traditional management approach as it helps to reduce the overall sludge volume. However, high emission rates of harmful oxides and dioxins coupled with intensive energy requirements rules it out as a sustainable practice.

2.5 Energy and nutrient recovery from wastewater sludge

Wastewater sludge utilization provides an exciting opportunity to recover energy and nutrients from wastewater treatment processes, as the energy contained in wastewater has been estimated to exceed treatment related energy by a factor of five [65]. Opportunities thus exist to make sludge treatment processes self-sufficient and sustainable, with the sludge acting as both the treatment feedstock and energy source.

Table 2.2 Energy in wastewater [66]

Constituent	Value	Unit
Energy content in wastewater, heat basis	41,900	MJ/°C•L
Chemical oxygen demand (COD) in wastewater	250 – 800	mg/L
Chemical energy in wastewater, COD basis	12 – 15	MJ/kg COD
Chemical energy in primary solids, dry	15 – 15.9	MJ/kg TSS
Chemical energy in secondary biosolids, dry	12.4 – 13.5	MJ/kg TSS

There has also been a shift in focus of wastewater treatment processes from nutrient removal to nutrient recycling. This is because nitrogen and phosphorus (some of the major constituted nutrients) has immense potential in the composting and organic fertilizer production sectors. This provides an opportunity to integrate multiple strategies towards ensuring the maximization of nutrient recovery from facilities, as this would aid the recycling of some precious resource [45].

Organic waste management processes can be largely grouped into biochemical and thermochemical processes, and are deployed with consideration to economics, feedstock availability and quality [67]. Biochemical conversion processes include anaerobic digestion, co-digestion, composting and biohydrogen production while thermochemical conversion processes include combustion, pyrolysis, gasification, wet oxidation, and hydrothermal processing.

2.5.1 Anaerobic digestion

Anaerobic digestion is considered by and large to be an environmentally friendly processing technique that converts organic waste into biogas and biosolids, with a noticeable reduction in gas emissions [68,69]. The biogas component is found to contain predominantly methane (60 to 65%) and carbon dioxide (30 to 40%), with minute concentrations of nitrogen and hydrogen sulfide [65].

Anaerobic digestion technology has been deployed in the treatment of waste streams from petrochemical industries, dairies, fisheries and municipal treatment facilities to produce biogas which has been re-integrated in boilers to help maintain mesophilic temperature regimes during the digestion process [70]. There are three major stages (or steps) in anaerobic digestion, namely hydrolysis, fermentation and methanogenesis with high preference for heterogenous organic materials as they are already hydrolyzed in most cases [71].

The hydrolysis stage is where complex organic compounds such as fat and cellulose are hydrolyzed into soluble compounds, thus creating substrate for fermentative bacteria to work on. The fermentation stage then kicks off, in which acidogenic and acetogenic bacteria ferment soluble organic compounds largely into acetic acid, hydrogen (H_2) and CO_2 [72]. The final stage, methanogenesis, makes use of methanogenic bacteria to convert the intermediates from the fermentation stage into methane, carbon dioxide and other gases [73,74]. Besides biogas, a solid-liquid mixture known as digestate is also produced which can be further separated into a nutrient rich liquid phase for fertilizer applications and a solid phase which can be composted for land amendment applications [75].

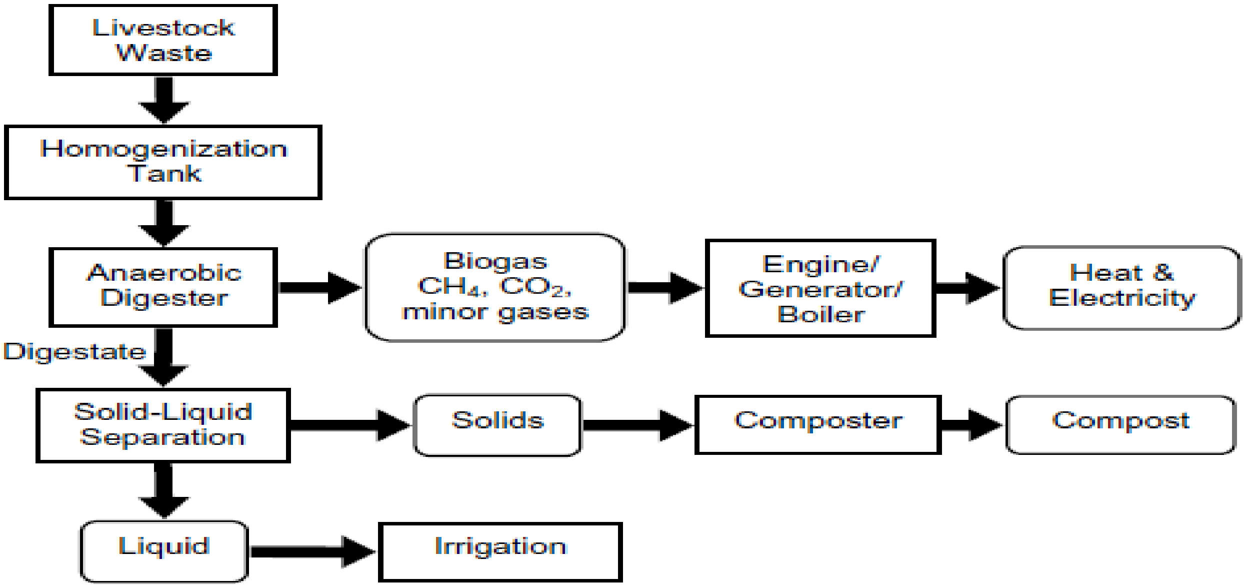

Figure 2.3 The anaerobic process [72]. Reprinted with permission from Elsevier.

2.5.2 Co-digestion

One limiting proponent of biogas production through anaerobic digestion is the readily available biodegradable portions of the solids, thus requiring the need for a way to maximize biogas production and optimize the treatment capacity of wastewater treatment plants. Co-digestion bridges this gap therefore, by adding readily available biodegradable feedstocks such as fats, oils and grease (FOGs) directly into the digester. This has been found to increase the C/N mixture and the nutrient base while increasing biogas yield [76,77]. High-strength organic wastes (HSWs) from food processing, brewing, animal farming industries have also been found to alter the rheology and other biogas properties which can impact the digester performance positively or negatively [78]. Significant challenges associated with anaerobic co-digestion include the inability to guarantee the biodegradability and nutrient balance of supporting feedstocks and the possibility of inhibiting materials being present [79].

2.5.3 Composting

Composting is generally a 3-stage (mesophilic, thermophilic, and cooling) process that converts sludge into carbon dioxide and water while raising its temperature to around 57–70 °C with subsequent destruction of the pathogenic microorganisms [80]. Composting is often integrated with pre-processing and post-processing steps which make the whole process economically viable thereby producing soil amendment solids [81]. Toxic organic compounds such as PAHs, PCBs and trinitrotoluene levels in sewage sludge have been found to be tremendously reduced on composting with residuals being either adsorbed in the compost or converted to intermediates [82-84]. Composting presents high operational costs for mixed municipal solid wastes; hence it requires that waste streams be source separated prior to feeding into treatment systems [85].

2.5.4 Biohydrogen production

Hydrogen gas has the potential to replace fossil fuels due to its clean burning and non-polluting nature. Biological synthesis of hydrogen from biosolids thus provides a strong case for the sustainable generation of a clean fuel [86]. The technology is still evolving however, and it involves a 2-stage photosynthetic and hydrogen production process, a photobiological process which is then followed by a fermentation process [72]. The dark fermentation process using glucose as a model substrate is presented in figure 2.4. The conversion process can be seen to produce pyruvate in the stage, while the second stage leads to the generation of acetyl coenzyme A (acetyl-CoA), carbon dioxide and hydrogen. Preliminary studies into this technology reveals that carbohydrate-rich waste materials yield better biohydrogen when compared with untreated biosolids [87,88].

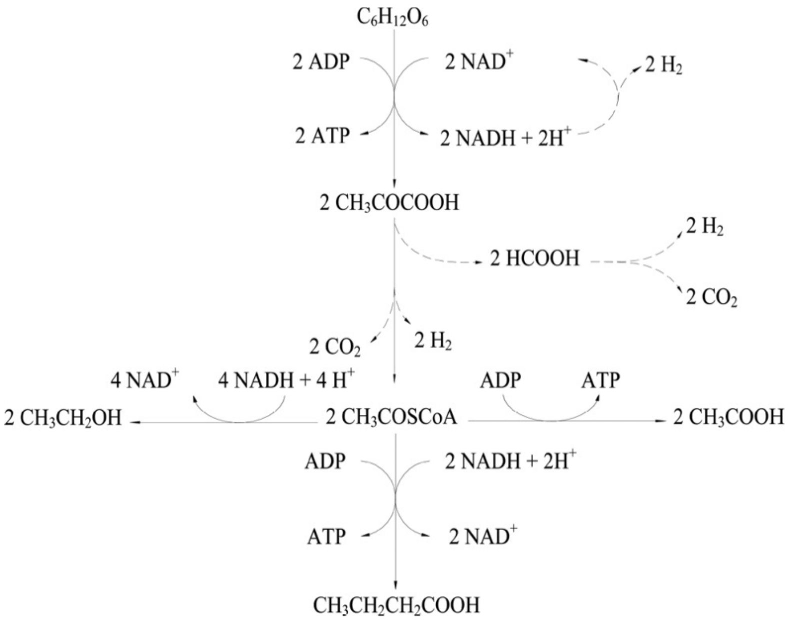

Figure 2.4 2-stage fermentative production of biohydrogen [78]. Reprinted with permission from Taylor & Francis.

2.6 Thermochemical conversion processes

Thermochemical conversion of wastewater sludge entails the use of catalysts and often high temperatures to valorize the feedstock in a matter of minutes or seconds, as compared to biochemical processes which could take several weeks or months [89]. Feedstock characteristics however play a determinant role in the quality of the products gotten, with total solids, volatile solids and ash content being some of the most important [72]. In conventional thermal treatment processes, metrics such as operating temperature and pressure, residence time and heating rate often determine the relative proportion of the derived phases [90]. Research has also been carried out on the integration of biological and thermochemical treatment techniques, and this has proven effective for very wet sludge samples [91].

2.6.1 Combustion

Combustion or incineration is the most established conversion technology for biosolids, and it is a high temperature complete oxidation process which converts biomass energy to heat. It is a dominant technology that significantly reduces the sludge volume while recovered most of its energy from the high temperature flue gases which are produced, and this can be subsequently used to generate electricity using a steam turbine [92]. Incineration is a widely developed technology in the United States, and about 17 – 25% of solids generated annually are valorized through this route majorly through multiple hearth incinerators or fluidized-bed incinerators [65]. Combustion processes proceed through three main stages of drying, devolatilization (or pyrolysis) and char combustion [89]. Challenges that have been encountered using incineration include the high moisture content of feed materials, and their high oxygen content [93]. There is not much support from the public regarding the use of incineration for solids valorization, as there are concerns about the high release rate of toxic contaminants such as dioxins, furans, nitrous oxides (NOx) [89]. Co-combustion of sludge with other waste streams is also possible, and it is currently being practiced in cement industries in Europe and North America. Furthermore, in Japan, sludge with a solid content of 50% has been found to be optimal for co-processing in cement kilns without any additional fuel [94]. In general, the combustion of wastewater solids has been made more efficient through advances in incinerator design. The presence of high amount of water however still serves as a huge impediment to effective energy recovery from sludge samples through this route.

2.6.2 Pyrolysis

Pyrolysis is a thermal decomposition of carbonaceous materials into solid, liquid, and gaseous components at temperatures ranging between 300 to 600°C in the absence of oxidizing environments [95]. The operating conditions of pyrolytic processes can be modified in such a way as to maximize the production of any of the components [96]. Based on residence time, pyrolysis can be classified as slow pyrolysis (longer), medium pyrolysis (10-20seconds) and fast pyrolysis (2seconds); with the highest bio-oil yield of 50-75% reported for fast pyrolysis [67]. Pyrolysis has been found to be effective for the conversion of biosolids due to its ability to destroy pathogens and reducing odor while generating the much-needed energy resource [97]. Apart from the oil produced, the generated char has been found to be a rich source of soil dependent nutrients such as nitrogen, phosphorus, calcium, magnesium, and potassium [98].

The major advantage of pyrolysis over other thermal treatment processes is the ability to produce a liquid that can be easily stored and transported to distant locations [96]. A major drawback of this technology however is the need for a pre-drying process which is expensive and leads to unattractive economics for wet feedstocks. Kinetics study of sewage sludge decomposition coupled with GC-MS analysis reveals that weight loss principally occurs around three temperature regimes: 250, 350 and 550°C [99,100]. The char phase derived from sewage sludge pyrolysis have been found to come short of adsorbent use requirements, but it holds immense potential in the elimination of sulfides and nitrous oxides generated during thermochemical processes [101-103]. The focus for the use of pyrolysis has been for the generation of liquid, and their yield have been studied through the catalytic and non-catalytic route. The non-catalytic process majorly adopts the use of nitrogen as the fluidizing gas in fluidized bed reactors although processes in fixed bed reactors and semi continuous vertical reactors [96]. Research on the catalytic pyrolysis of sewage sludge have been somewhat limited however due its similarities with lignocellulosic and lipid feedstocks which have been extensively studied. Both feedstocks majorly researched the use of zeolites and gamma-alumina respectively as catalysts, with the focus on the reduction of the oxygen content of the generated oil in a bid to increase the hydrogen to carbon (H/C) ratio. Apart from feedstock characteristics, operating properties such as solids feed rate, sludge particle size and distribution, reaction atmosphere have been found to affect the respective yields [96].

Recent advents in the pyrolytic process have led to the study of microwave-assisted pyrolysis, which make use of microwave in lieu of electric furnaces and this has been observed to increase syngas yield [104,105]. The conversion of sewage sludge through pyrolysis has been extensively studied and well documented, with products ranging from solid adsorbents to gases [106-108]. Most pyrolysis studies using sewage sludge for liquid production purposes have made use of dry sludge samples, as it has been found that most of the moisture in the sludge is translated to the liquid phase [109].

2.6.3 Gasification

Gasification is a thermal conversion process that generates syngas (mainly H_2 and CO, with H_2O, CH_4, N_2 and tars as impurities) at temperature regimes of 500 – 1600°C and pressures of around 1 to 60 bars in controlled air setting [110]. Syngas is a very important fuel for steam or heat generation or to produce clean hydrogen gas and synthesis of important chemical compounds although the effectiveness of this syngas depends on its specific heating value [111]. Apart from effectively handling pollutants and pathogens, gasification has the comparative advantage of eliminating treatment steps such as stabilization, digestions and composting which tend to be capital intensive [112]. Most innovative syngas generation processes involve the integration of dewatering, drying, gasification and electric power generation stages in that sequence, and it has been found to lower the natural gas requirement as compared to incineration by 83% [113]. Apart from energy recovery, it is also possible to generate methanol by flowing the generated syngas from sludge gasification to methanol production facilities [114].

Supercritical water gasification (SCWG) is a novel gasification technique that makes use of the supercritical properties of water at points higher than the critical points of temperature and pressure to convert wood and agricultural wastes for the focal generation of hydrogen gas. This technique is suitable for high moisture content feedstocks such as sewage sludge, although reactor plugging has been documented in some experiments [115]. The gasification of wastewater sludge has been studied, and the quality of the derived syngas has found to be affected most by temperature [116], pressure [117] and catalyst amount [118].

2.6.4 Wet oxidation

Wet oxidation is a thermochemical process that converts waste streams from petrochemical, chemical and pharmaceutical industries which cannot be efficiently valorized through conventional biological treatment processes [119]. It involves the addition of oxygen to these waste streams to generate carbon dioxide and other low-molecular weight hydrocarbons at temperature regimes of 180 - 315°C and pressure intervals between 2 – 15 MPa, and subsequently converts halogenic and sulfuric compounds present into halides and sulfates respectively [119,120]. Supercritical Water Oxidation (SWO) builds up on this and entails the complete oxidation of organic matter (up to 99.99%) in about a minute, very much less than the 30 -120 minutes required for wet oxidation. However, higher degrees of corrosion are experienced during SWO although significant amount of heat is recovered which can be used for electricity generation while the gaseous products (CO_2 and N_2) are commercially viable [121]. Wet oxidation, particularly sonolysis, has been found to be an effective pre-treatment method for municipal sludge. This helps the disintegration of sludge components into simpler particles, thus aiding biodegradability and methane production [122].

2.7 Hydrothermal conversion technology

Hydrothermal conversion is a low-temperature and high-pressure process that breaks down biomass into smaller compounds using the thermal properties of water or another suitable solvent [123]. It is particularly suitable for wet feedstocks as there is no need for a pre-drying step, which is critical in other thermo-chemical processes such as pyrolysis. However, hydrothermal processing often requires sophisticated and expensive reactors to ensure high throughput and energy efficiency [124]. Conversion processes start with a depolymerization stage where feedstocks are broken down into monomer units, and reactions could proceed to higher order state reactions where char formation is predominant. Depending on the feedstock of investigation, it might be necessary to integrate solvents that could help lower these state reactions and effect product yields which correlate to their dielectric constants [125]. Whereas catalysts are not critical in pyrolytic reactions, they are essential for hydrothermal processing to help control reaction temperatures, to improve product and quality, and to enhance reaction kinetics [126]. It has however been observed that while alkaline catalysts improve heavy oil yield and reduce the formation of residues, acidic catalysts are renowned for decreasing the reaction temperature and residence time [127,128]. Depending on parameter adjustments, it is possible to influence the conversion of feedstocks into solids (hydrothermal carbonization), liquids (hydrothermal liquefaction) and gases (hydrothermal gasification). However, there is a need to fully understand how water behaves in a hydrothermal medium prior to assessing the different processing pathways.

2.7.1 Sub- and Supercritical properties of water

Water is termed a universal solvent due to its ability to dissolve almost oil solute except oil, paraffin, and wax. Its properties at high temperature favor liquefaction processes, as it can act as a reaction medium, a reactant and as a catalyst [129]. The phase diagram of water represents the properties of water across three fundamental phase regions and is given below (Figure 2.5). The critical point (or water triple point) shown in this diagram represents a point where water co-exists in three phases. Water above this critical point (374 °C and 22 MPa) is said to be at supercritical conditions while water beneath is termed as sub-critical. At subcritical conditions, a two-phase liquid-gas configuration is noticed while supercritical water conditions ensure that water stays in a macroscopically homogenous stage due to a change of nature from a polar compound to a pseudo polar compound [130,131].

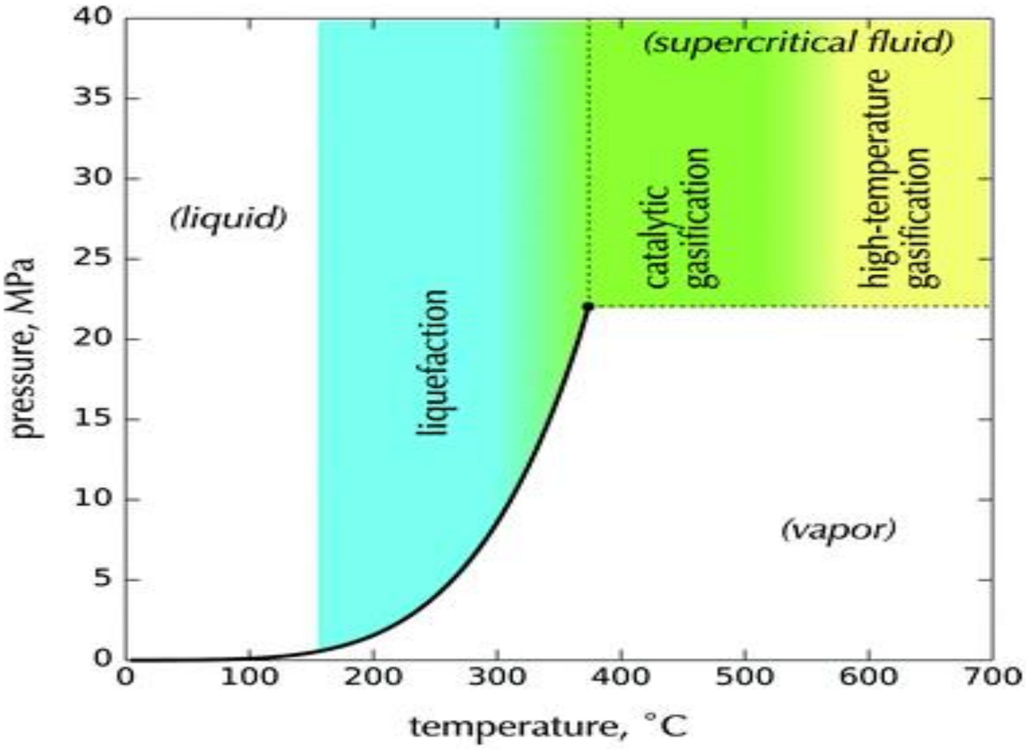

Figure 2.5 Pressure (P) vs Temperature (T) phase diagram of water [124]

Another important property of water worth mentioning around this critical region is the dielectric constant, which is the relative permittivity and it affects the Coulombic force of attraction between two point charges in the water molecule. The dielectric constant decreases on increasing temperature and completely drops to one, making it entirely possible for biomass substances to become entirely miscible with water at critical or supercritical conditions.

The ionic is the product of the molecular concentration of the hydronium (H_3O^+) and hydroxyl (OH^-) ions that are in equilibrium with non-dissociated water molecules [132]. The fluctuation of this property with respect to temperature and pressure helps to determine the negative logarithm of the product of these ionic concentrations (pk_w) which in turn favors biomass hydrolysis at 250°C and 24MPa, and favors bond cleaving free radical reactions at supercritical conditions [131]. This explains why hydrothermal gasification reactions are the favored outcome at supercritical temperatures while liquefaction reactions occur at subcritical regions (Table 2.3).

Table 2.3 Properties of supercritical and subcritical water [130]

Properties	Subcritical Water	Supercritical Water	Supercritical CO_2	Subcritical Steam
Temperature (°C)	25	400	55	150
Pressure (MPa)	0.1	30	28	0.1
Density (kg/m^3)	997	358	835	0.52
Dynamic viscosity (μ) (kg/m s)	890.8×10^{-6}	43.83×10^{-6}	0.70×10^{-6}	14.19×10^{-6}
Diffusivity of small particles (m^2/s)	$\sim 1.0 \times 10^{-9}$	$\sim 1.0 \times 10^{-8}$		$\sim 1.0 \times 10^{-5}$
Dielectric constant	78.46	5.91		1.0
Thermal conductivity (λ) (W/m k)	607×10^{-3}	330×10^{-3}		28.8×10^{-3}
Prandtl number ($C_p\ \mu/\lambda$)	6.13	3.33		0.97

2.7.2 Hydrothermal Carbonization

Hydrothermal carbonization (HTC) is a thermal processing technique focused on the conversion of feedstocks such as sewage sludge, municipal solid wastes and lignocellulosics into carbonaceous material at temperatures below 225°C and pressure below 2MPa [133]. It is a viable alternative to biochemical conversion processes (anaerobic digestion, co-digestion and composting) primarily due to its shorter duration of operation (few minutes) and the relatively smaller size of processing facilities [134]. Biochar is becoming a very vital resource, due to its capability of being a direct substitute for fossil-based coal in the generation of synthesis gas and for land amendment purposes [135].

Through the integration of thermogravimetric analysis (TGA) with Fourier transform infrared spectroscopy (FTIR), it is possible to characterize the gaseous products emanating from the disintegration of solid materials. This procedure suggests that a higher concentration of HTC char in single or multicomponent mixtures would favor the generation of more carbon dioxide (CO_2) in lieu of carbon monoxide (CO), thus ensuring the production of less toxic gases during the combustion of densified solid fuels [136]. HTC of sewage sludge has been found to be very effective in the removal of heteroatoms (O, N, S), with more successful removal being recorded on increasing temperature and retention time [137]. The release of sulfur-containing gases into the atmosphere during the combustion of char has been a matter of intense debate however, with about 90% of sulfur in the sludge being found in the char [138].

2.7.3 Hydrothermal Gasification

Hydrothermal gasification is a conversion process that occurs near or above critical conditions of temperature and pressure, generating mainly methane, hydrogen, and carbon dioxide. The presence of catalysts in the conversion process has been found to lower the reaction temperature and subsequently increase the yield of gases [139]. It is however important to optimize the amount of catalyst used however, in order to prevent issues relating to corrosion, plugging, and fouling [140]. The high organic nature and presence of high water content in sewage sludge requires a slight modification of gasification procedures, resulting in supercritical water gasification (SCWG). SCWG can process sludge with moisture contents up to 94% with higher reaction temperatures however needed for complete gasification. A reduction in the moisture content has also found to affect the proportion of gaseous compounds, with the effect most pronounced for carbon dioxide while moderate reduction in yield is observed for hydrogen and methane [141]. The hydrothermal gasification of municipal sludge has been found to be mostly impacted by catalyst type [142], reaction temperature [143] and residence time [144].

2.7.4 Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is a hydroprocessing technique that converts biomass materials into biocrude by predominantly making use of the properties of water at sub and supercritical conditions of temperature and pressure. HTL reactions normally take place at temperatures between 280 to 380°C, and residence times from a few seconds (fast HTL) to 60 minutes with a pressure regime of 7 – 30 MPa [145]. This ensures that water remains in the liquid phase, and the observed products have lower oxygen and moisture contents as compared to products from pyrolysis [146]. A typical pathway for hydrothermal liquefaction involves an initial hydrolysis (sugar production) stage where almost all hemicellulose is converted while decreasing amounts of lignin and cellulose conversion, which is then followed by a series of depolymerization, cracking, condensation and repolymerization [147]. Apart from the produced biocrude oil, a heavily mineralized char phase, a gas phase and a nutrient filled aqueous phase are produced. To make use of the biocrude oil as a direct crude oil substitute however, there is a need for an upgrading step due to the presence of large amount of oxygen (10-20%), nitrogen (4-6%) and sulfur [148]. The HTL was largely considered in its inception as a direct replacement for fossil produced crude oil, with the first significant work carried out by the Pittsburg Energy Research Center (PERC) in the early 1970s.

The agitation at the time was due to fluctuating oil prices, but the significant progress was almost forgotten when oil prices boomed again. There has been a renewed interest in liquefaction systems, majorly bench and pilot scale processes and this being spearheaded by the Pacific Northwest National Laboratory (PNNL) and The University of Sydney. Companies, on the other hand, tend to often have proprietary systems development. However, Genifuel Corporation (USA) is currently carrying out pilot tests into the development of continuous HTL systems for renewable fuels and clean water production [149]. Table 2.4 reviews the major works that have been carried out regarding the liquefaction of sludge to date. It shows the impact that process parameters, catalyst loading, and pretreating can have on the quality of the produced biocrude. Furthermore, it provides insight into beneficial uses of byproducts of the hydrothermal liquefaction process (i.e. gas, biochar and aqueous fraction).

2.7.5 Influence of operating conditions on HTL yield

There have been pronounced effect of operating conditions such as temperature, pressure, residence time and integration of catalysis on the yield produced for different fractions of sewage sludge. These conditions are biomass dependent because while the optimum temperature for product yield maximization is 340°C for manure; it was suggested that 275-300°C works best for sewage sludge [150-152]. Pressure is very important for maintaining a single-phase during liquefaction reactions, although lesser impacts are seen at supercritical conditions [153]. The degree of pre-processing has also been found to affect the produced bio-oil yield. Raw digested sludge of different pre-treatment steps (waste activated, primary and mixed) have been found to have higher oil yields which have averaged 43% [154]. The solvent used for the extraction of oil from the char and aqueous phases have also been found to affect the amount of oil recovered after rotary evaporation, with dichloromethane found to recover more biocrude than other studied solvents [155]. The effect of catalysis on liquefaction reactions have also been widely reviewed. Different catalyst affects product yields in various ways, just as the liquefaction pathways change with respect to acidic, neutral and alkaline conditions [156]. Apart from the type of catalyst, catalyst loading also affects the liquefaction products as a decrease in oil yield was noticed for increasing in the loading rates of alkaline catalysts [155]. The HTL process, however, impacts the overall composition of final fuel products, as hydrotreating experiments on waste oil and waste plastics at 400°C and 425°C have shown [157]

Table 2.4 Previous work done on the hydrothermal liquefaction of sewage sludge

Year	Type of Sludge	Catalyst	Observations	Reference
1987	Digested sludge, raw sewage activated sludge, raw primary sludge and raw mixed sludge.	Na_2CO_3	Raw primary sludge and raw mixed sludge were identified as the optimum sludge type, achieving yields of up to 43% at 300°C and 12MPa working pressure. Catalyst addition did not affect the yield (48% with 5wt. % loading) by much, but increased produced oil's HHV	Suzuki *et al.* [154]
1992	Mixture of primary and waste activated sludge	None	Acid-base extraction fractionation of sludge produced at 330°C, 15.5 MPa and 60 min holding time revealed 2% weak acid fraction (phenolics), 20% basic fraction (pyridines, pyrazines, quinolines, amines and methylphenylacetamide) and 56% neutral fraction (aliphatics, alicyclics, alcohols, ketones, aromatics, sulfur , nitrogen and oxygen heterocyclic compounds)	Dote *et al.* [153]
2010	Primary, secondary and digested sewage sludge	None	Supercritical treatment of the different sludge types at varying temperatures (400 to 450°C) and holding time (20 to 120 min) noticed the favorable formation of phenols and variety of phenol-based compounds at low temperatures and short residence times. Gases were however favored at higher temperatures, but the residence times had little or no effect on the gas yield.	Zhang *et al.* [157]

Year	Type of Sludge	Catalyst	Observations	Reference
2011	Secondary sludge	K_2CO_3 & Heterogeneous ZrO_2	One step catalytic conversion of sludge discovered 330°C and 25MPa (residence time of 5mins) to be the optimum conversion conditions. K_2CO_3 was observed to be more effective, as it increased the heavy oil yield up to 30% within 300 – 330°C temperature regime.	Hammerschmidt *et al.* [158]
2011	Digested sludge	None	The influence of wastewater feedstock composition on the liquefaction of digested sludge was studied under the operating conditions of 300°C, 10 – 12 MPa, 30 min residence time and 20% solids loading. The feedstock contained primarily 51% of neutral detergent fiber (NDF), 42% of crude protein and 36% of acid detergent fiber (ADF). 9.4% oil yield was recorded and was attributed to large carbohydrate content due to high hemicellulose and lignin content.	Vardon *et al.* [159]
2012	Sewage sludge	K_2CO_3 & Heterogeneous ZrO_2	The bio-oil and aqueous phase produced from subcritical conditions (350°C and 25MPa) were analyzed using GC-MS, HPLC and an incorporated HPLC-TOF-MS method. Sample prepared using DCM solvent gave highest peak areas, but this was associated with some background noise which was not noticed during the use of THF. In general, polar aprotic solvents (DCM and THF) were found to recognize more compounds when compared with polar protic compounds (ethanol and methanol)	Villadsen *et al.* [160]

Year	Type of Sludge	Catalyst	Observations	Reference
2013	Sewage sludge	None	A comparative liquefaction study was done to study the effect of structural compositions on products derived from sewage sludge, lignocellulosic biomass (rice straw) and algae. Higher yields were observed for sewage sludge, despite having lesser organic matter content.	Huang *et al.* [161]
2014	Sewage sludge	Sewage-sludge based activated carbon (SSAC)	SSACs synthesized from pyrolysis of sewage sludge at 550 and 650°C at 60, 90 and 120 minutes were used to liquefy dewatered sludge at 350 and 400°C. The liquefaction was found to redistribute the type of solid metals found in the char phase, with Cu and Zn being detected at both temperatures. The highest yield was however recorded at 350°C.	Zhai *et al.* [162]
2014	Dewatered sewage sludge	None	The liquefaction study was carried out using two different solvents, ethanol and acetone at operating temperatures of 280, 320 and 360°C. Higher yields were achieved with acetone as solvent, with the highest oil yield achieved at 360°C, being 46%. It was also noticed that most of the heavy metals present in the sludge were concentrated in the char phase (up to 90%), with the amount in the oil phase steadily increasing at increasing liquefaction temperature for most of the heavily metals present except for zinc which showed no clear trends.	Leng et al. [163]

Year	Type of Sludge	Catalyst	Observations	Reference
2014	Dewatered sewage sludge	None	The effect of three solvents (ethanol, methanol and acetone) on liquefaction yields was studied at temperatures ranging from 260 to 380°C at 20 minutes holding time. Although the highest oil yield was attained with acetone, the overall conversion efficiency was in the order of methanol>ethanol>acetone. Methanol and ethanol also favored mainly ester compounds in the bio-oil while acetone yielded more ketones and nitrogen compounds.	Huang *et al.* [164]
2015	Primary settling wastewater	None	The use of wastewater from treatment facilities to grow algae (Galdieria sulphuraria) was studied at target temperatures within 180 - 300°C range, and possible nutrient take-up during recycled aqueous phase (AP) runs. Higher biomass productivity was noticed during the recycled run, and the recorded nutrient levels of 80 mg NH_3-N $L^{-1}$and 20 mg phosphate L^{-1}were much higher than the levels observed in the origin wastewater stream.	Selvaratnam et al. [165]
2015	Secondary activated sludge	None	Liquefaction experiments were carried out within 260 to 380°C temperature range, and the oil was further upgraded by microemulsion technology. Bio-oil composition analysis (GCMS) revealed the presence of esters, ketones, alcohols and phenols when acetone was used as solvent, and predominantly esters when methanol or ethanol was used as solvent. The bio-oil obtained using methanol was found to be relatively easier to upgrade, as ethyl esters were found to be the least diesel-solvable compounds.	Leng et al. [166]

Year	Type of sludge	Catalyst	Observations	Reference
2015	Dewatered sewage sludge	CaO	Liquefaction experiments carried out between 200 to 380°C showed different results based on the CaO/C ratio, in which gas production reduced on increase in CaO catalyst. Among other noticed trends was a decrease in gas concentration on increase in sludge moisture content, while TOC and COD levels decreased on increase in temperature.	He et al. [167]
2016	Sewage sludge	None	A sequential extraction method for removal of metals in sewage sludge samples prior to liquefaction was studied for its effect on products. The experiments were carried out using ethanol as the solvent, and it was discovered that the demetalization step did not reduce the organic matter content (yield) of the respective fractions. However, the resulting bio-oils and bio-chars were discovered to be cleaner possibly due to the removal of heavy metals such as Cu, Zn, Cr, Pb and Cd.	Leng et al. [168]
2017	Primary sludge	None	Biocrude from the liquefaction of primary sludge at 345°C and 2900psig was compared with petroleum crude oil and shale oil. FT-ICR-MS analysis revealed that sewage biocrude was compositionally more similar to shale oil than petroleum crude, with few heteroatom classes detected. It was generally deduced however that petroleum and shale oil are compositionally dissimilar to sewage sludge biocrude, with over 85% of compounds identified using electrospray mass spectra not present in petroleum or shale oil.	Jarvis et al. [169]

Year	Type of sludge	Catalyst	Observations	Reference
2017	Sewage sludge	K_2CO_3, Na_2CO_3, HCOOH, Ru/C and MoO_3-CoO/γ-Al_2O_3	Isothermal (400°C, 60min) and Fast (500°C, 1min) liquefaction of sludge with 50% additive loading rate recorded higher yield for the fast process. Furthermore, the added catalysts were observed to have reduced the oil yields while promoting the gasification of the sludge (except for the carbonates).	Qian et al. [155]
2017	Dewatered sewage sludge	None	The NOx emission removal potential of the hydrothermal liquefaction of sludge was carefully studied to ascertain the redistribution of nitrogen (N) in the liquefaction products. Selection of temperatures within 150 - 300°C and residence times within 30 – 480 mins revealed that only 20% of N was retained in the char phase while nearly all of remaining 80% was dispersed in the other phases as various forms including ammonium nitrogen, pyrole-N, pyridine-N and quartenary-N.	Zhuang et al. [170]
2018	Primary sludge, Secondary sludge and digested solids	None	Liquefaction tests carried out on the three sludge types at temperature regimes of 300 -350°C and 20MPa pressure revealed a bio-oil yield ranging from 25 to 37%, with composition and quality comparable with algal biomass biocrude. An HTL-CHG process was also suggested for the reduction of the chemical oxygen demand (COD) of aqueous products, with a 99.9% removal rate documented	Marrone et al. [171]

Year	Type of sludge	Catalyst	Observations	Reference
2018	Primary and Secondary sludge	K_2CO_3	A novel method involving the use of lignocellulosic biomass filters in the generation of high dry matter sludge was developed. The filter cake developed was then subsequently liquefied at 340°C and a residence time of 20 minutes. The biocrude generated showed superior qualities than those produced from the use of the alkali catalyst and from co-liquefaction, with a higher energy recovery (75%).	Biller et al. [172]
2019	Sewage sludge	Sewage sludge ash	Microalgae (Chorella) and sewage sludge were co-liquefied at 340°C, an initial H_2 pressure of 0.3MPa and a residence time of 30 mins using different feedstock ratios under different ash conditions. A yield increase of 4.7 wt.% was recorded when a 1:1 mixing ratio of the feedstocks with a 3.6% decrease in char yield, while pyrolysis-state ash catalysts helped to increase C and H contents and HHV while reducing the N and O contents.	Xu et al. [173]
2019	Sewage sludge	Potassium and sodium salt (-OH/ -CO_3)	Rice straw and wood sawdust were co-liquefied with sewage sludge at temperature intervals (20°C) between 200°C and 320°C, residence times between 0mins and 60mins with no initial pressure applied. Increase in residence time was found to slightly increase the amount of oil formed, while the use of an ethanol-water co-solvent was found to increase the oil yield by almost 10 wt. % for the rice straw co-liquefied feedstock. There was generally an observed reduction in the nitrogen and oxygen contents and an increased formation of phenolic compounds on using co-feedstocks.	Huang et. al [174]

Year	Type of Sludge	Catalyst	Observations	Reference
2019	Dewatered secondary sludge	None	The effect of pre-treatment using different surfactants on the liquefaction of dewatered sludge was studied at 340°C and a residence time of 40 mins. A higher bio-oil yield (47.6%) was recorded, and this was found to correlate with the relative ease of releasing the bound water in the sludge. A significant reduction in the bio-oil nitrogen content (6.1% to 2.9%) was also recorded after subcritical water pretreatment.	Yang et. al [175]
2019	Dewatered sewage sludge	None	The hemicellulose, crude protein, cellulose, lignin and lipid/oil fractions in the sewage sludge was liquefied from 200 - 450°C in order to investigate the decomposition of chemical compositions. Hemicellulose was found to have the highest conversion efficiency (99.1%), with bio-oil found to be the main constituents at 200 – 350°C while gas and char were favored at 350 – 450°C.	Su et. al [176]
2019	Sewage sludge	None	The molecular composition of HTL wastewater produced at temperatures of 170°C and 320°C at a residence time of 1 hour was studied vis-à-vis its transformation during anaerobic digestion. Liquefaction wastewater at higher temperatures was found to contain lower molecular weight dissolved organic matter with an enhanced composition of nitrogenous substances.	Hao et. al [177]

2.8 Bio-oil properties

The properties of bio-oils generated from sewage sludge varies with respect to operating conditions and sludge characteristics

Table 2.5 Elemental Analysis and Higher Heating Value comparison between different sludge HTL bio-oils

Operating T oC, t min	300°C, 30min	340°C, 40min	350°C, 19 min	350°C,20min	400°C, 60min	Crude Oil
Sludge Type	Digested, Anaerobic	Sewage	Secondary	Sewage	Sewage	
Reference	Vardon et al. [159]	Yang et al.[175]	Marrone et al. [171]	Huang et. al [161]	Qian et. al [155]	[184]
C, wt.%	66.6	70.7±0.3	72.5	72.51	72	83 – 87
H, wt.%	9.2	10.1±0.2	8.7	9.44	8.76	10 – 14
N, wt.%	4.3	6.1±0.3	5.1	6.96	5.04	0.1 – 2
S, wt. %	0.97	1.3±0.2	0.90	negligible	1.1	0.05 – 6
O, wt.% *	18.9	12.9±0.2	6.5	11.09	7.68	0.05 – 1.5
H/C	1.66	1.71	1.44	1.56	1.46	
O/C	0.21	0.14	0.07	0.11	0.08	
HHV(MJ/kg)	32.0	32.2±0.3	34.8	36.14	38.0	44.5
Yield, wt.%	9.4	23.7	24.8	39.5±1.16	26.8±1.2	
Solids Content, %	20	15	9.71	14.4	15	

**: calculated by difference

Table 2.5 itemizes the ultimate analysis and higher heating values of HTL bio-oils generated from different types of sludge, and compares to typical petroleum crude values. This clearly shows the presence of heteroatoms (N,S and O) in the sludge bio-oil, and could lead to toxic emissions if not removed. This provides a big obstacle to the co-processing of sludge and petroleum crudes, hence the need for upgrading processes.

2.9 Upgrading of Bio-oil

A handful of research papers have been published on the upgrading of HTL bio-oil produced from different types of sludge [178-183]. While HTL is a thermal depolymerization process seeking to break down biomass macromolecules into water-containing soluble organic compounds, upgrading is concerned with the improvement in the overall quality of the bio-oil. Some of the undesirable properties in the bio-oil that necessitates the need for an upgrading step include high oxygen and nitrogen content (which leads to a reduced heating value), high water content, high viscosity, high acidity and thermal instability [178]. In order to obtain high value chemicals through the bio-oil upgrading technique, there needs to be a planned and systematic approach. Different bio-oil upgrading techniques exist (Table 2.6), primarily due to challenges associated with the conversion of feedstocks using respective routes e.g. catalyst deactivation during the esterification of pyrolytic lignin [179].

Bio-oil from different sludge types were upgraded using microemulsion technique, as a result of methyl esters being the dominant component [180]. The emulsion was carried out using different bio-oil/biodiesel ratios through a series of mixing and centrifugation and the products were analyzed using a blend of thermodynamic analysis and kinetic studies. The biodiesel/bio-oil ratio of 10 was found to be the most suitable for upgrading, with an observed shift in decomposition to higher levels. There was also a noticed reduction in the hybrid activation energy of the blend, offering insight into the possibility of co-processing both feedstocks on an industrial scale.

Table 2.6 Advantages and challenges associated with some bio-oil upgrading techniques [178]

Upgrading method	Process condition	Reaction description	Technical feasibility	
			Pros	Cons
Solvent addition	Mild conditions, needs polar solvents	Increases HHV and reduces viscosity	Simple	No chemical reaction to remove undesired compounds within bio-oil
Emulsification	Mild conditions, needs surfactant	Emulsifying bio-oil with diesel or biodiesel using surfactant	Simple	Energy consumption, non-removal of undesired compounds
Esterification	Mild conditions, needs alcohol	Chemical reactions like esterification and acetalization	Relatively simple, mild conditions, low cost of alcohol	Does not remove N-containing compounds
Supercritical fluids (SCFs)	Relatively high T and P, need for organic solvents	Promotes reaction using density, viscosity and diffusivity of SCFs	Effective to increase HHV and reduce viscosity	Needs high-pressure equipment and expensive solvents
Hydrotreating	Relatively high T and P, need for catalysts and high-pressure hydrogen	Hydro-deoxygenation, hydrogenation without simultaneous cracking or partial cracking	Removes N, O and S as NH_3, H_2O and H_2S. Increase HHV.	Needs high-pressure equipment. High coking and catalyst deactivation.
Catalytic cracking	Relatively high T and P, need for catalysts and high-pressure Nitrogen	Hydrogenation with simultaneous cracking	Produces large number of light products	Needs high-pressure equipment. Catalyst deactivation.

2.10 Hydrotreating of sewage bio-oil

Hydrotreating has been extensively developed in the oil and gas industry for the treatment of crude and has been adapted to biorefinery approaches for the removal of heteroatoms. This is attainable due to the fundamental chemical knowledge that on subjecting compounds to high pressure environments (up to 20 MPa) at around 300 - 450°C coupled with the addition of an hydrogen donating source, it is possible to remove O, N and S compounds in bio-oil [164]. Some of the reactions that take place during hydrotreating is shown below:

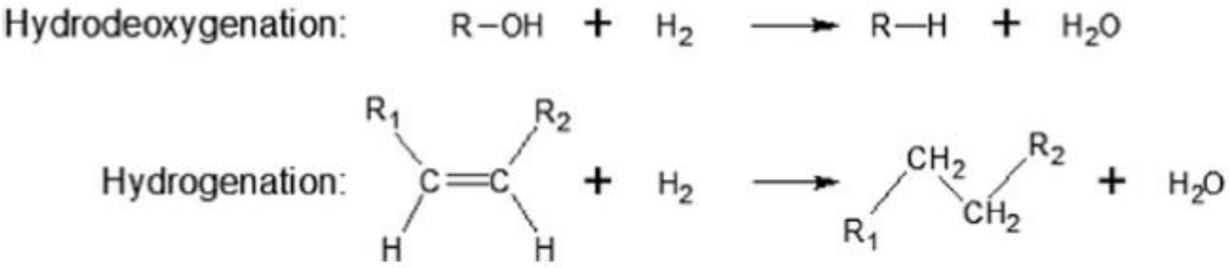

Figure 2.6 Hydrotreating reaction mechanism [164]

Hydrotreating reaction rates are efficient due to the presence of catalysts that help in the cracking process, and a number have been reported in literature. Hydrotreating studies on sludge bio-oil have been carried out using catalysts such as $CoMo/\gamma - Al_2O_3$ [172] and pre-sulfided $NiMo/Al_2O_3$ [181-183]. Although this is somewhat limited, it provides insight on the effect of catalysts on the upgrading process. High carbon yields were reported in the hydrotreated crude, with an overall increase in the quality of the oil, although this lead to a decrease in the overall oil yield due to the conversion of the removed heteroatoms to products in other phases [171,182]. This was validated by GC-MS analysis, which recorded a major decrease in the heteroatom peak area (from 70% in the sludge HTL bio-oil to about 10% in the oil upgraded at 400°C at a residence time of 4hours) while supporting the generation of more hydrocarbons (15% peak area in the HTL oil to 70% in the hydrotreated oil at the same operating conditions).

FTIR-MS analysis of sludge-derived HTL bio-oil and hydrotreated oil generally reveals a conversion of heteroatoms into a more desirable product containing majorly hydrocarbons. This hydrotreated product was however found to contain lesser monoatomic oxygenated compounds and lower carbon numbers than shale oil [183]. Simulated distillation of hydrotreated sewage bio-oil samples also revealed that the increase in the proportion of oil in the gasoline (<193°C) and light diesel (272 – 321°C) ranges with a noticeable increase in the residues formed as compared to sewage sludge HTL bio-oil [182].

2.11 Conclusions

Hydrothermal liquefaction (HTL) is a promising pathway for the conversion of municipal sludge. The overall effectiveness of the process depends on the design and synthesis of catalysts targeted towards improving the overall quality of fuel. The HTL product yield depends on the type of catalyst, the catalyst loading, the liquefaction temperature, influence of solvents and co-solvents, and on sludge pre-treatment. Much work on the liquefaction of municipal sludge have made use of alkali-based catalysts such as Na_2CO_3, K_2CO_3, CaO and heterogenous ZrO_2**.** Na_2CO_3 was particularly effective, resulting in a yield of 48wt. % at 300ºC and 5wt. % catalyst loading. Increase in the catalyst loading did not increase the yield by much, but it resulted in a decrease in the heavy oil fraction of produced oil. The overall yield and product quality was also found to be impacted by the use of solvents. The use of acetone as a co-solvent has been found to yield biocrude fractions as high as 46 wt. % at 360ºC, although with more ketones and nitrogen compounds observed. Large heteroatom (N, S and O) content is a highlight of municipal sludge biocrudes, with nitrogen contents of about 6 wt. % reported. This presents significant challenge to co-processing with petroleum-based crudes, thereby making biocrude upgrading a necessity.

Conventional CoMoS and NiMoS have been found to be effective catalysts in removing heteroatoms from municipal sludge biocrudes, thereby producing high quality fuels with 1 wt. % O, <005 wt. % S and acid number less than 0.01 mg KOH/g. The manner of catalyst preparation (sulfiding) and leaching of S into produced oils however remain a challenge. There is therefore a need for further research into low-cost catalysts with higher activity and stability for both liquefaction and upgrading processes. Pre-treatment approaches such as the dewatering of sludge using surfactants and sequential extraction for the removal of metals also appear to improve the heteroatom challenge of sludge biocrudes.

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Chapter 3

Hydrothermal liquefaction of municipal sludge

3.1 Abstract

This study presents the comparison on the effect of temperature and solids content on the product yield and fuel quality of municipal sludge hydrothermal liquefaction (HTL) products with and without red clay. HTL was carried out on three sample types: Pre-dried sludge (“PD”, dewatered secondary sludge that was further pre-dried prior to use), Secondary sludge (“Sec”, after aerobic digestion but before running through the belt press) and Thickened sludge (“Tk”, secondary sludge that had gone through aerobic digestion and mechanical belt pressing to increase the solid content at the treatment station).

HTL was carried out at 300ºC and 325ºC, with a reaction residence time of 1hr and a continuous stirring speed of 95RPM maintained in all experiments. Highest oil yield of 37.7±1.6 wt.% was obtained when thickened sludge was liquefied at 325ºC, while the highest char yield of 20.6±1.6 wt.% was obtained when catalyzed secondary sludge liquefaction was conducted at 325ºC.The higher heating value of the biocrudes ranged from 24.2±0.3 MJ/kg (catalyzed secondary sludge oil produced at 300ºC) to 35.0±0.8 MJ/kg (pre-dried sludge oil produced at 300ºC). The total acid number (TAN) was lowest (13.1±0.3 mg KOH/g) when thickened sludge biocrude was produced at 300ºC, and was highest (19.8±1.6 mg KOH/g) when secondary biocrude produced was processed at 325ºC. Integration of the red clay catalyst significantly improved the TAN value of biocrudes. The obtained char products from the catalyzed liquefaction processes had a low HHV due to higher amount of ash (75.2±0.3 to 81.0±0.2 wt. %). The produced aqueous phase was particularly rich in ammonia-nitrogen, although slightly lower concentrations were found in the catalyzed aqueous products, due to redistribution to other product phases.

3.2 Introduction

The shift to cleaner and environmentally friendly sources of fuel has received rapid endorsement in recent times due to increased public awareness to the adverse impacts of fossil-based energy and strong policy frameworks. With the forecasted increase in anthropogenic carbon dioxide emissions to 43.08 billion metric tons in 2050 (from current levels of 35.6 billion metrics), there exists an opportunity to further reduce emissions through the use of renewable waste feedstock such as wastewater sludge [1].

Wastewater sludge is a nutrient-rich byproduct of biological wastewater treatment processes. The treatment of municipal waste prior to discharge to water bodies prevents algal blooms, prevents the spread of waterborne diseases, and ensure compliance to safe water drinking standards [2,3]. Publicly owned treatment works (POTWs) utilize biological, chemical, and thermal stabilization processes to separate municipal solid wastes (MSWs) and sewage sludge from the wastewater stream. However, techniques (such as digestion, landfilling, incineration, and thermal drying) currently used to manage the solid byproducts have not been effective in removing contaminants (such as hydrogen sulfide, leachates, fly ash and carbonaceous residue) and odor. Development of processes that overcome the issues (contaminants, odor, and non-biodegradability) with MSW and sewage sludge is needed [4].

Hydrothermal processing technology provides an option for processing sewage sludge, due to its suitability for feedstocks that have high moisture content [5]. The use of supercritical water to process feedstocks for bio-crude production was first attempted at the Pittsburgh Energy Research Center (PERC) in the United States, making use of cellulosic and waste biomass sources [6]. Hydrothermal liquefaction (HTL) is a type of hydrothermal biomass processing technology that is carried out at temperatures of 280 to 380°C, pressures of 7 – 30MPa and residence times that vary from a few seconds (fast HTL) to 60 minutes [7]. Typical HTL reactions of lignocellulosic biomass involve an initial hydrolysis stage which results in the production of sugars, followed by a series of depolymerization, cracking, condensation and repolymerization [8]. HTL is becoming a more attractive approach when compared to current municipal solids treatment processes, due to documented efficacy of this technology in removing bioactive compounds (such as florfenicol and bisphenol) [9] and perfluoroalkyl acids [10].

The liquefaction of sewage sludge varies slightly from other wet wastes because it is a composite mixture of various compounds such as proteins, cellulose, grease and fats. While different sewage sludge types exist (primary, secondary, activated, and digested), constituents such as protein, nitrogen, phosphorus, and silica are quite common in all [11]. Studies on the HTL of sewage sludge are quite extensive; the effect of various operating parameters such as catalysts [2,12] solvents [13,14] and feedstock composition [5,15] have been reported previously. HTL has been found to be generally effective in the conversion of sewage sludge, the challenge however remains the improvement of the overall quality of the various product phases. The sequential extraction technique was used to de-metalize sewage sludge prior to liquefaction experiments, in order to produce cleaner biochar and biocrude with no heavy metal components. This resulted in organic matter loss in the sludge however, although a higher biocrude yield of 45% was obtained at higher temperatures (350-375ºC) [13].

Of increasing importance in waste treatment processes is a circular economic approach in reusing wastes generated from these facilities [16]. This ensures that all the liquid, solid and gaseous fractions from energy processes are effectively managed and recycled thereby reducing waste management challenges. Researchers in the HTL processing route for MSWs are proactive in ensuring that all the different byproducts (particularly char phase) are put into use. To strengthen this bioeconomic concept, activated carbon catalysts derived from biochar were found to increase the density of produced biocrude and also reduced the heavy metals in solid residue [17]. An improved bio-oil yield and energy density was also observed while subsequently lowering the risk of heavy metals such as Pb and Zn at operation conditions of 350°C, 30 minutes residence time and 20% catalyst loading using HTL biochars and ethanol solvent [13].

HTL has also proven versatile in the conversion of other sludge wastes. Refinery oil sludge with high moisture content (92.6%) was successfully converted at 290ºC and 10wt. % sludge loading, thereby generating a bio-oil yield of 45.5% at 65 minutes residence time [18]. Higher bio-oil yield of 58 wt. % was observed by using oil mill wastewater sludge at optimum conditions of 280°C and 30 minutes [19].

Catalysts, when integrated with HTL reactions, reduces reaction activation energy, and increases biocrude yield [2]. However, the catalyst cost is a major hindrance to the scale-up of HTL technology, with costs capable of attaining $1.3 million per annum for a 110 dry ton/day sludge HTL plant [20]. There is therefore a need to conduct studies that assess the effectiveness of readily available and low cost catalysts in improving biocrude quality.

Red clay is formed as a result of weathering and washing away of rock particles over a long period. Red clay was used as a catalyst in the liquefaction of food waste, and its primary role in the promotion of reaction rates was confirmed [21]. The synergistic effect of the acid and base sites present in the heterogeneous red clay was also found to result in higher energy recovery (45.4±4.0 %), much higher than those reported using constituent oxides. The HTL processing of sewage sludge using red clay as a catalyst has however not been explored. This study therefore performs a comparative analysis of the effects of red clay catalyst and different sludge moisture contents (5%, 15% and 20%) and types (Secondary and Thickened) on the fuel properties and byproduct characteristics of hydrothermal liquefaction products. Sub-critical temperatures of 300°C and 325°C were studied, and all the four phases (biocrude, gas, aqueous and biochar) of the resulting liquefaction products were analyzed.

3.3 Materials and methods

3.3.1 Feedstocks, Chemicals and Reagents

HTL experiments were performed on three types of sludge: pre dried sludge (PD: secondary thickened sludge but dried prior to use), secondary sludge (Sec: after aerobic digestion but before running through the belt press) and thickened sludge (Tk: secondary sludge collected after the belt press). All the samples were obtained from the H.C. Morgan Pollution Control Treatment plant located in Auburn, Alabama USA. The secondary sludge ("Sec" hereafter) was retrieved just after secondary treatment processes onsite, while the thickened sludge ("Tk" hereafter) was obtained after activated sludge feeds were subjected to polymer (polydyne) coagulative separation and mechanical belt pressing activities. The samples were immediately stored at 4°C. All stored samples were analyzed and processed within one month of collection, in order to prevent microbial degradation effects from extended storage periods. The thickened sludge was dried at 105°C for 24h and ground before experiments. The total solid content, ash content and volatile matter content of each sample were determined according to EPA method 1684, ASTM E1755 and ASTM E872 method, respectively. The higher heating values of the sludge feedstocks was determined by using an oxygen bomb calorimeter (IKA model C2000, Wilmington, NC, USA) while the elemental compositions were determined with a vario MICRO cube from Elementar (Ronkonkoma, NY, USA) and a method was based on ASTM D5373-02.. The red clay used in this study was collected from a local construction site at Auburn University (Auburn, Alabama USA). The red clay was prepared by drying at 105°C for 24h after which it was crushed. This study used the portion of the crushed red clay sample that passed through a 595 µm sieve. In-situ XRD of the red clay was performed using a theta-theta diffractometer (Proto AXRD, Ontario, Canada) with an X-ray Kα line from a Cu target with 40kV at 30mA, with a 1°C/min temperature ramp rate and two 10s diffractogram snapshots taken every 10°C. Ultrapure (Type 1) deionized water was used for liquefaction experiments and was obtained from Synergy Ultrapure Water Systems. Isopropyl alcohol (laboratory grade) was obtained from VWR, and dichloromethane (CH_2Cl_2) of ≥ 99.80 % grade quality was obtained from Sigma-Aldrich. Ultra-high purity nitrogen, helium and ultra-zero air (99.999%) was obtained from Airgas Inc. Hardened ashless Whatman Filter papers (CAT NO. 1005-055) obtained from VWR (Atlanta, GA) were used for filtration purposes.

3.3.2 Liquefaction experimental procedure

HTL experiments were performed in a Parr Instrument Company high pressure reactor (model 4578). The reactor has a capacity of 1800mL and is equipped with a controllable stirrer, PID controlled heating furnace, pressure gauge and J-type thermocouple. HTL experiments were performed at 300°C and 325°C. The residence time in the reactor for each sample was 60 min, with each sample being continuously mixed by a magnetic drive agitator at 95RPM. For the liquefaction of PD samples, 120g of dry sludge was combined with 480g of DI water thus maintaining the biomass loading at 20% in all experiments. For the Sec and TK samples, 600g of sample was loaded into the reactor in each experiment in order to study the effect of solids content (6% and 15%) on the yield and properties of liquefaction products. In all catalyzed reactions, 40g of red clay was added. The reactor was purged with nitrogen thrice in order to remove any trapped air within the reactor, and then pressurized to an initial pressure of 95psi (0.65MPa) with nitrogen. After the 60 min reaction residence time, the reactor was cooled to room temperature (~22°C) via water circulation through a cooling coil located within the reactor. Gas samples were collected in tedlar bags for composition analysis. The procedure utilized to separate the remaining three phases (solid, aqueous and biocrude) is described in the next section. All experiments were performed in triplicates.

3.3.3 Product separation

Figure 3.1 shows the flowchart of the procedure used in this study. The four HTL products are biochar, biocrude, gas and aqueous phases. The content of the reactor (biochar, biocrude and aqueous phases) was poured into a beaker. To ensure that all of the contents were retrieved as practical as possible, the reactor and stirrer were rinsed with 200mL of methylene chloride (DCM) and combined with prior extracts. The contents of the beaker were then vacuum filtered with Whatman No. 5 (2.7µm) paper after which the biochar was recovered, dried in an oven at 105°C for 24 h to determine the biochar yield. Decantation was then used to remove aqueous phase from the liquid portion obtained from the filtration step, after which the DCM and biocrude mixture was separated by rotary evaporation using an IKA rotary evaporator maintained at 60°C and 720mbar for about 1 hour.

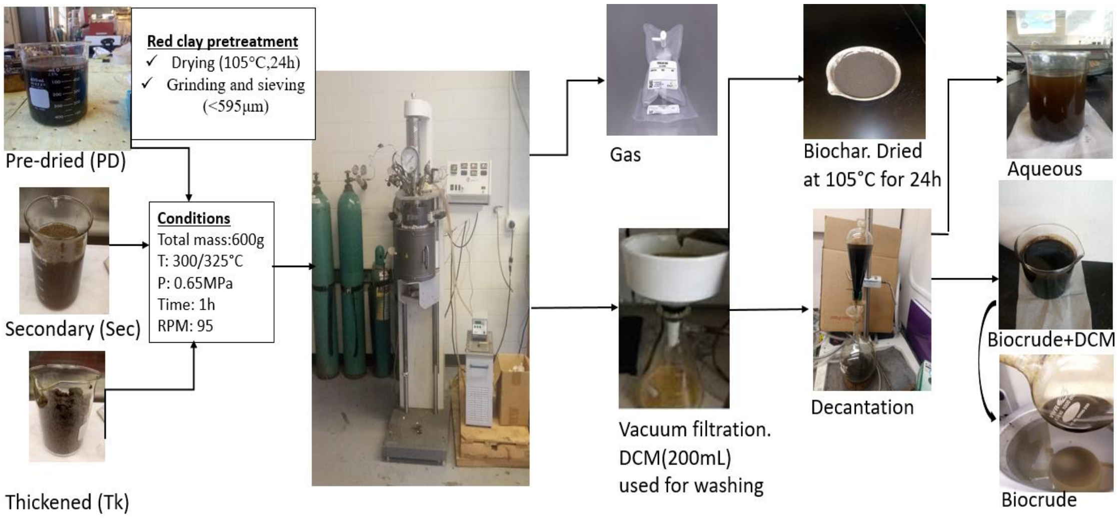

Figure 3.1 Process flow diagram of product separation

A mass balance analysis was carried out for each experimental procedure in order to calculate the yield of each phase fraction recovered from the HTL process. The mass of the gaseous phase was calculated as the difference between the pre-liquefaction and post-liquefaction mass of the reaction mixture in the batch reactor vessel. The various phase calculations were calculated as follows:

$$\text{Gas yield d.b, ash free (wt. \%)} = \frac{\text{Final mixture mass - Initial mixture mass}}{\text{Mass of dry sludge- Ash content (g)}} \times 100 \qquad (1)$$

$$\text{Biocrude yield d.b, ash free(wt. \%)} = \frac{\text{Mass of oil obtained (dry basis)}}{\text{Mass of dry sludge-Ash content (g)}} \times [100\text{-Moisture\%}] \qquad (2)$$

$$\text{Biochar yield d.b, ash free(wt. \%)} = \frac{\text{Mass of solid char (dry basis)}}{\text{Mass of dry sludge-Ash content (g)}} \times 100 \qquad (3)$$

$$\text{Aqueous yield (wt. \%)} = 100 - (\text{Gas yield} + \text{Biocrude yield} + \text{Biochar yield}) \qquad (4)$$

The experimental plan for the liquefaction study was executed as shown in the table below:

Table 3.1 Experimental design for liquefaction study

Sample	300°C		325°C		Total experiments
	Catalyst	No catalyst	Catalyst	No catalyst	
PD	✓	✓	✓	✓	12*
Sec	✓	✓	✓	✓	12*
TK	✓	✓	✓	✓	12*

*: three repetitions each

3.3.4 Biocrude analysis

The physical and chemical properties of the different biocrude samples were measured using various analytical procedures. Elemental compositions were determined using a vario MICRO cube from Elementar and a method based on ASTM D5373-02. The water content (wt. %) was determined using the Karl-Fisher (KF) titration on a V20 volumetric KF titrator from

Mettler Toledo using the ASTM D6869 method, ash content (wt. %) was measured according to ASTM E1755 standard method, total acid number (TAN, mg KOH/g) was determined using the ASTM D664-18e2 method on a Mettler Toledo T50 titrator, the higher heating value (HHV) was measured in MJ/kg using an IKA C2000 model oxygen bomb calorimeter while density and viscosity measurements (at 40°C) were performed using an Anton Paar SVM 3000 Stabinger Viscometer.

The chemical composition of the biocrude was identified using a gas chromatography-mass spectrometry (GC-MS) (Agilent 7890 GC/5975 MS) equipped with a DB-1701 column. Prior to analysis, 5 wt.% of the biocrude was dissolved in CH_2Cl_2 (DCM) after which each sample was injected into the column. The initial temperature of the column was set at 40°C, and was maintained for 6min after which it was ramped to 280°C at 6°/min and held for 10mins. Ultra-high purity helium was used as the carrier gas and the flow rate was maintained at 1.76ml/min. Each biocrude sample was analyzed twice after which the peak areas were averaged. Compounds were identified by using the NIST (National Institute of Standards and Technology) mass spectral library. The compounds were largely grouped into alkanes (including straight chain, branched chain and cyclic), alkenes (straight chain, branched chain and cyclic), alkynes (straight chain, branched chain and cyclic), oxygen containing compounds (O-compounds; majorly carboxylic acids, furans, alcohols and esters), nitrogen containing compounds (N-containing; majorly adamantanes and pyrazoles), nitrogen and oxygen containing heteroatoms (N-O compounds; majorly oximes, oxy-pyrimidines and acetamides), aromatics (benzenes, phenols, indoles, etc.) and other compounds (including rare compounds such as thiophenes, disulfides and kryptons) .These divisions were based on the parent compounds, and adjoining derivatives. In complex cases of compound characterization, precedence was given to the parent compounds.

Additional functional group information was obtained from FTIR spectroscopic data. FTIR spectra was collected by applying ~20mg of biocrude sample on a Thermo Nicolet iS10 equipment (Thermo Scientific, Waltham MA) from 4000 to 400 cm^{-1} and averaged over 64 scans using Omnic software. Before the use, background scans were collected at ambient temperature after cleaning the ATR surface with isopropyl alcohol.

Simulated distillation was performed using an Agilent 7890A gas chromatography (GC) equipment equipped with an Agilent DB-2887 column (10m × 0.53mm × 3.00μm) and FID detector using the ASTM D2887 method. Sample preparation was done by diluting biocrudes with 1-2 wt.% of carbon disulfide (CS_2). The inlet was set at 350°C with a split ratio of 1:2, and the FID detector was also set at 350°C. The heating program commenced with a starting temperature of 40°C and was then ramped to 350°C with a heating rate of 20°C/min while the helium carrier gas was set at a constant flow rate of 14 mL/min. The time obtained from the sample injection were translated into temperature using the ASTM D2887 method calculations. The boiling point were categorized into gasoline (<193°C), jet-fuel (193°C-271°C), light diesel (272°C-321°C), heavy diesel (321°C-425°C) and vacuum gas oil (425°C-564°C).

3.3.5 Aqueous phase analysis

The aqueous phase samples were filtered using a 0.2μm paper and subsequently stored at 4°C prior to analysis. All analysis was performed in triplicates. The Total Nitrogen (TN) and Total Organic Carbon (TOC) concentrations in the aqueous phase were analyzed using a TOC-L analyzer attached with a TNM-L unit from Shimadzu Corp., Japan. The samples were diluted 100 times using ultrapure water and measured in the autosampler. The Chemical Oxygen Demand (COD) was measured using the Hach 8000 method on a purchased HACH COD assay kit in a DRB200 sample digestor, while a Spectronic® $20D^{+}$ (Thermo Scientific, Waltham MA) was used to measure the COD concentrations. The pH readings of the various HTL aqueous phases were taken using an Oakton pH 510 Series Ph/mv/c instrument. (Eutech Instruments, Singapore). The soluble cations and anions in the aqueous phase were measured using a Shimadzu Prominence High Pressure Liquid Chromatography equipment using a conductivity detector. 20µl of prefiltered samples was injected into the columns in all cases. The cations present in the aqueous phase were separated using a Dionex CS12 column (4 × 250mm) coupled to a CS500 self-regenerating suppressor supplied with 59mA. The column flow rate was maintained at 1 mL/min of 20mM methanesulfonic acid in nanopure water. The anions were separated using a Dionex AS22 column (4 × 250 mm) coupled to anAS500 self-regenerating suppressor supplied with 26 mA. The column flow rate was also maintained at 1mL/min of 4.5 mM sodium carbonate and 1.5 mM sodium bicarbonate in nanopure water. The column oven was set to 28°C in all cases while the peak integration was done on the Shimadzu LC Solutions software. The chemical composition of the aqueous phase was analyzed using a prior acid dissolution followed by GC-MS analysis [22].

3.3.6 Gas phase analysis

The composition of the gaseous phase samples collected with tedlar bags was measured using an INFICON Model 3000 Micro Gas Chromatograph (GC) equipped with a thermal conductivity detector (TCD). The installed columns included Molsieve (30µm × 320µm × 10m), PLOTU backflush (30µm × 320µm × 3m), PLOTU fixed (30µm × 320µm × 6m) and a Variable OV1 (2µm × 150µm × 14m). Ultra-high purity helium was used as the carrier gas, and the measured gases included hydrogen, saturated and olefinic hydrocarbons (C_1 – C_5 and C_{6+} grouped peaks) and permanent gases (O_2, N_2, CO and CO_2).

3.3.7 Biochar analysis

The char from the hydrothermal liquefaction of sewage sludge was measured for its higher heating value (HHV), ash content and elemental composition using the methods described earlier.

3.3.8 Statistical analysis

Results were expressed as mean ± S.D. Differences between groups was analyzed using ANOVA and Tukey test using the SAS statistical software package (Version 9.4, SAS Institute Inc., Cary, NC) for windows. A p-value of less than 0.05 was considered to be statistically significant.

3.4 Results and discussion

3.4.1 Characterization of sludge samples

Table 3.3 presents the proximate and ultimate analyses of the sewage sludge samples used in this study. Both sludge samples can be seen to have similar ash and higher heating values. The ultimate analysis also suggested that both samples were compositionally similar, although a higher oxygen content was observed in the thickened sludge. A possible reason could be the effect of polymer use in the sludge dewatering process, which has been found to result in the release of extracellular polymeric substances (EPS) such as tyrosine/tryptophan amino acid [23,24] .The pre-dried sludge has the higher elemental carbon and hydrogen, which translated to the higher heating value of 16.5±0.1MJ/kg. The measured properties are similar to previously studied sludge samples [25-26], although higher C contents have been reported [27-28] due to pretreatment processes which included sieving and mechanical pulverization.

Table 3.2 Proximate and ultimate properties of sewage sludge feedstocks

Feed	**VM (wt.%)**	**Ash (wt.%)**	**Total Solids**	**Ultimate Analysis**					**HHV d.b**
			(d.b %)	**C**	**H**	**N**	**S**	**O**	**(MJ/kg)**
Sec	70.3^{a}± 0.1	23.0^{a}± 0.1	6.2^{b}±1.1	36.8^{a}± 0.0	6.0^{a}± 0.1	6.1^{a}± 0.1	0.8^{a}± 0.1	27.5^{b}±0.2	16.2^{a}±0.1
Tk/PD	69.0^{b}± 0.1	23.0^{a}± 0.1	15.2^{a}±0.1	35.3^{b}± 0.2	5.76^{a} ±0.0	5.9^{a}± 0.1	0.8^{a}± 0.0	29.3^{a}±0.3	16.5^{a}±0.1

Different alphabets in the superscript of each column denote that the values are significantly different for each sludge type. Values after ± denote standard deviation.

The XRD pattern of the red clay is shown in Figure 3.2. The spectra was obtained in the 2 theta range from 20 to 80°. The red clay can be seen to compose of a variety of oxides, namely aluminum oxide, iron oxide, ilmenite, and silica oxide. The intensity of silica can be seen to be the highest in the catalyst, and this can impact its performance in a liquefaction medium. HTL of food wastes using these metal oxides independently reported elemental carbon contents of 62.3 wt. % (SiO_2) and 71.3 wt. % (Fe_2O_3), compared to 67.7 wt. % when red clay was used [21].

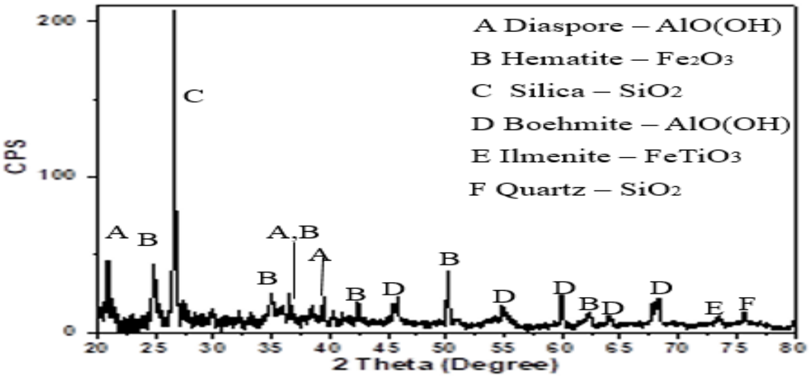

Figure 3.2 XRD pattern of red clay used in this study

3.4.2 Liquefaction yields

Figures 3.3 and 3.4 show the yields of the different phases produced from sewage sludge liquefaction at 300°C and 325°C respectively. Biocrude yield significantly increased with increase in temperature ($p<0.0001$) which can be attributed to the synergistic effect of biomass fractionation in the liquid phase, and the reduced dielectric constant of water [29,30]. The highest biocrude yield of 37.7±1.6 wt. % was observed at 325°C and was achieved in the thickened sludge, while the lowest yield of 21.5±1.3 wt. % was recorded in the secondary sludge liquefied at 300°C. The biochar yield reduced on increased temperature, which can be attributed to the favored production of gaseous and biocrude components at higher temperatures [6]. This consequently meant that the yield of biochar and aqueous reduced with increased temperature as a result of more organic products being converted to biocrude and gas. Generally, temperature can be seen to favor more conversion in high solid content (pre-dried and thickened sludge) feedstocks. The biocrude yield in the thickened sludge is higher than that of the pre-dried sludge despite having lower solids content (15%). A possible explanation for this can be that the pre-drying step results in the loss of organics that could easily be transformed to the biocrude phase, leaving behind organic fractions that require higher temperatures or suitable catalysts to affect their conversion.

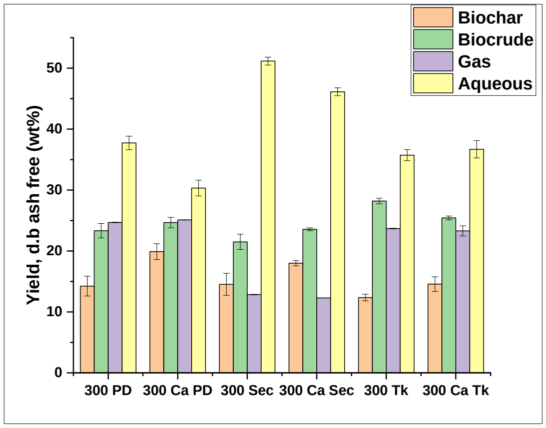

Figure 3.3 HTL product yields at 300ºC

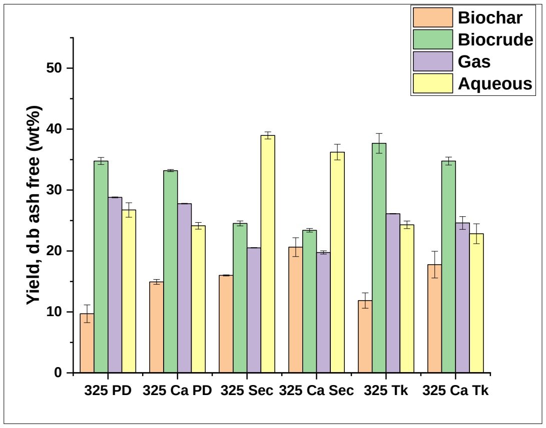

Figure 3.4 HTL product yields at 325ºC

The use of red clay as a catalyst did not significantly improve the biocrude yield, but it reduced the gaseous and aqueous phase yields. In all cases, the use of red clay as a catalyst resulted in higher char fractions, due to metallic distribution effects [13]. In order words, a combinative effect of red clay and increased temperature helped to channel the organic yield towards the biocrude and gaseous phases. The highest biocrude yield obtained at 325°C is lower than the yield obtained in literature from similar feedstocks [5,27]. An explanation for this is the slightly higher C contents reported in the raw feedstocks used (47.8 wt. % and 49.6 wt. % respectively), thus signifying the importance of organic carbon in optimum biocrude yield.

3.4.3 Biocrude characterization

The biocrude generated from the hydrothermal liquefaction of sewage sludge has been shown from literature to have consistent properties with algal biocrude products [5,31]. The possibility of generating valuable resource from negative feedstocks such as sewage sludge presents an opportunity for possible biocrude commingling with algal generated resource and consequently make for a strong case for integration in energy distribution efforts. The measured biocrude properties of the sludge used for this study and the effects of using a red clay as a catalyst is presented below.

3.4.3.1 Effect of red clay on the proximate and ultimate properties of biocrudes

Figure 3.5 presents the elemental composition and kinematic viscosity for the biocrudes generated from the three types of sludge studied in this work. The carbon and hydrogen content in the biocrudes ranged from 58.3±0.3 to 74.1±0.9 wt.% and 8.4±1.0 to 14.3±0.2 wt.% respectively. The highest oxygen content of 18.0±1.6 wt. % was obtained in the biocrude derived from the liquefaction of pre-dried sludge at 325°C, indicating that the highest amount of oxygenated compounds are present in these biocrude. The presence of a considerable amount of elemental oxygen in the biocrude phases signify a high degree of unstability, which will result in toxic emissions and creation of high amounts on cokes in vehicle engines if these biocrudes were to be used directly as liquid transportation fuels.

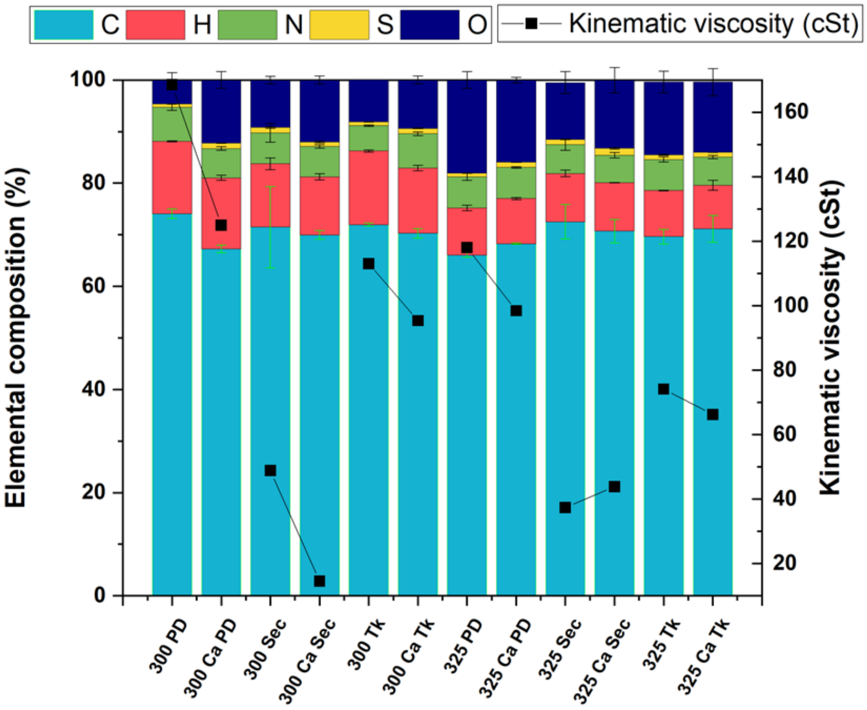

Figure 3.5 Ultimate analysis and kinematic viscosity plot for biocrudes

The C, H, N and O contents in the red clay catalyzed biocrudes were comparable to the uncatalyzed reactions and previous studies [5,32] but with higher sulfur content. The kinematic viscosity of the biocrude samples at 40ºC ranged from 14.5 to 165.6cSt, and there was significant impact of the catalyst support here. Reduced viscosity was observed in almost all samples which is a great advantage for transporting biocrudes of this nature over long distances, as it is less likely to polymerize when compared with more viscous biocrudes from the non-catalytic HTL. Table 3.4 presents some physical properties of the obtained biocrudes. The higher heating values ranged from 24.2±0.3 MJ/kg to 35.0±0.8 MJ/kg. These values are within the range of similar biocrudes [5,25], and are slightly lower for biocrudes obtained from the catalyzed reactions, possibly due to the slight reduction in the elemental carbon present in the biocrudes. There was also considerable ash production from the catalyzed experiments due to more metallic contribution from the red clay to the biocrude phase. The total acid numbers (TANs) were very much lower than those reported in literature [5], possibly due to an overall reduction in the acid strength of the carboxylic acids produced over red clay. The amount of moisture in the resulting biocrudes were lower in the catalyzed experiments, due to a possible migration of hydrogen species to the gaseous and aqueous phases. While the red clay did not increase the biocrude yield the quality (kinematic viscosity, moisture and TAN) can be seen to significantly improve.

Table 3.3 Proximate properties of biocrude samples

Samples	**Moisture (wt. %)**	**HHV, d.b(MJ/kg)**	**Ash (wt. %)**	**Density (g/ cm$^{3)}$**	**TAN(mgKOH/g)**
300 PD	4.4^{a}±0.3	35.0^{a}±0.8	0.1^{e}±0.01	1.1	19.3^{a,b}±0.4
300 Ca PD	1.0^{c,d,e}±0.1	34.9^{a,b,c}±0.7	0.4^{c,d}±0.10	1.1	17.4^{c,d}±0.1
300 Sec	1.8^{b,c,d,e}±0.6	25.0^{h}±0.1	0.1^{e}±0.05	1.1	17.0^{c,d,e}±0.2
300 Ca Sec	1.5^{b,c,d,e}±0.2	24.2^{h}±0.3	0.3^{c,d}±0.01	1.1	14.9^{f,g}±0.1
300 Tk	1.9^{b,c,d}±0.8	30.9^{f}±0.2	0.3^{d}±0.01	1.1	13.1^{h}±0.2
300 Ca Tk	1.1^{c,d,e}±0.3	29.6^{g}±0.2	0.4^{c,d}±0.01	1.1	13.9^{g,h}±0.4
325 PD	2.8^{b}±1.0	34.3^{a,b}±0.3	0.6^{b}±0.02	1.0	15.7^{d,e,f}±0.8
325 Ca PD	1.9^{b,c}±0.2	32.1^{d,e}±0.6	1.5^{a}±0.16	1.0	13.8^{g,h}±0.3
325 Sec	0.6^{e}±0.1	32.8^{c,d}±0.2	0.5^{b,c}±0.01	1.1	19.8^{a}±1.6
325 Ca Sec	1.1^{c,d,e}±0.1	31.3^{e,f}±0.3	1.5^{a}±0.02	1.1	17.9^{b,c}±0.3
325 Tk	1.0^{c,d,e}±0.1	33.1^{b,c,d}±0.3	0.4^{c,d}±0.00	1.1	18.6^{a,b,c}±0.4
325 Ca Tk	0.6^{d,e}±0.1	34.0^{a,b}±0.1	0.4^{c,d}±0.01	1.1	15.7^{e,f}±0.2

Different alphabets in the superscript of each column denote that the values are significantly different for each sludge type. Values after ± denote standard deviation.

3.4.3.2 Effect of red clay on the compositional properties of biocrudes

Figure 3.5 presents the FTIR spectra of biocrudes obtained from this study. The biocrudes from both 300 and 325ºC reaction temperatures, and from the two reaction types (red clay catalyzed and uncatalyzed) have very comparable spectra, thus suggesting the presence of similar functional group distribution. The spectral categorization and interpretation were based on prior studies [33-35].

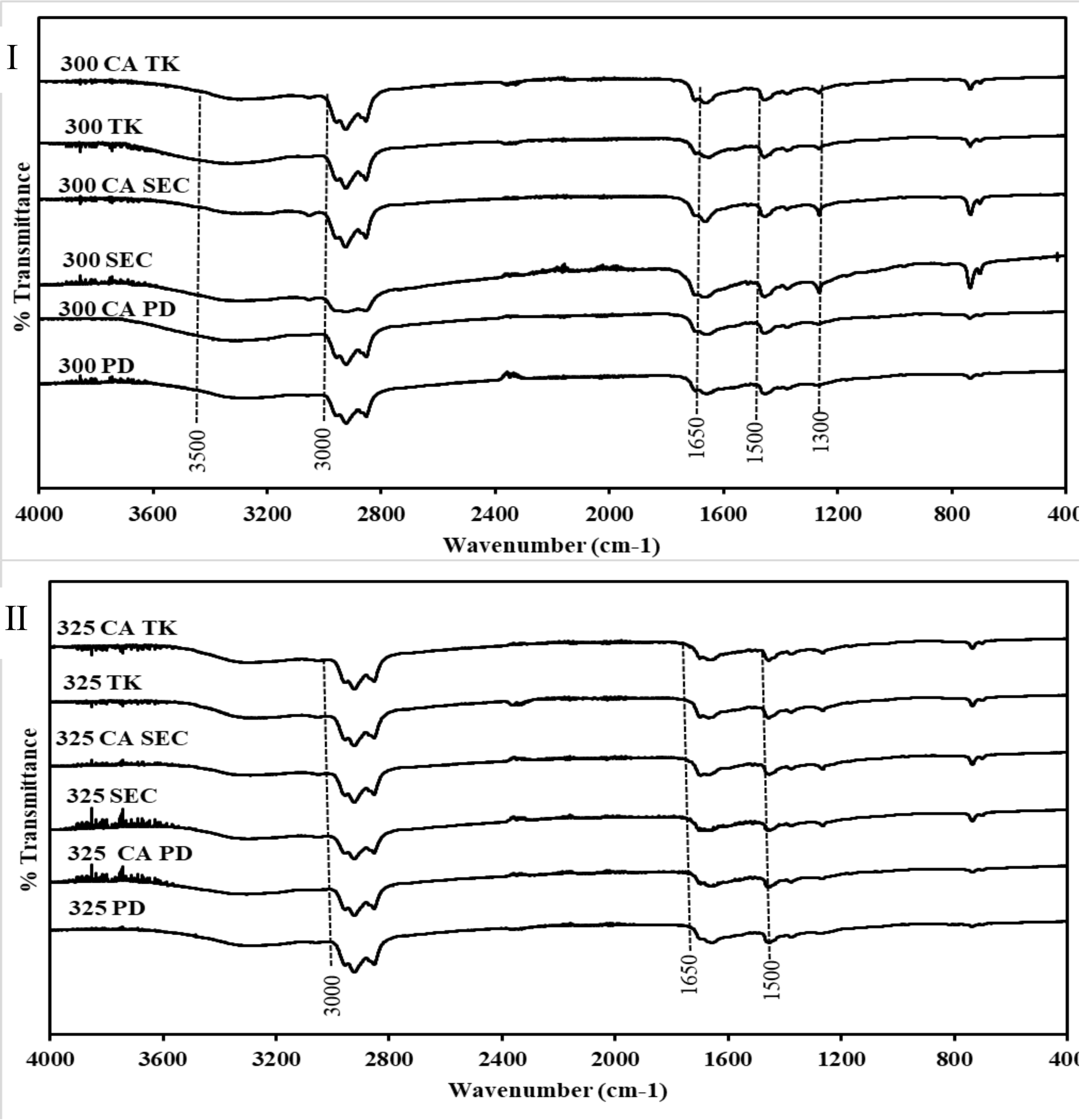

Figure 3.6 FTIR spectra of HTL biocrudes produced at 300ºC (I) and 325ºC (II)

The transmittance peaks observed between 3500 and 3200 cm^{-1} correspond to stretching vibrations. This confirms the presence of O-H (compounds such as alcohols and carboxylic acids) and N-H (amines and amides) functional groups. The aromaticity and possible unsaturation of these biocrudes is suggested through the presence of C-H stretching bands observed within 3000 to 2800 cm^{-1}. The strong peaks observed around 1650cm^{-1} corresponds to C=O stretching bands which could suggest the presence of compounds such as acids, ketones and aldehydes. The presence of amide groups in the biocrudes was confirmed by the peaks observed within 1600 to 1500 cm $^{-1}$. CH_2 and CH_3 vibrations (1500 to 1300 cm^{-1}), C-O and C-O-C stretching vibrations (1200 to 800 cm^{-1}) and possible cycloaliphatic stretching (beyond 800cm^{-1}) are also some of the similar functional groups noticed in the biocrudes. The common compounds with their relative peak areas across all biocrudes obtained at 300°C can be seen in Table 3.5, and this did not vary significantly from the biocrudes obtained at 325°C. There is a need for proper heteroatom classification in order to assess the ease of upgrading these biocrudes into liquid transportation fuels. The aromatic, oxygenated, and nitrogen-oxygen compounds can be seen to have a high peak area across all different biocrude types. The highest peak area reported for nitrogen containing compounds (N-compounds) of 12 % in the secondary sludge was lower than documented (21%) in a higher temperature study in literature [28], suggesting the tendency of free nitrogen to form fairly stable nitrogen compounds with high bond energies at higher temperatures.

The most detected compound across all samples were oxygen compounds (majorly 9-Octadecenoic acid, (E)- and Octadec-9-enoic acid), which is very much like algal based biocrudes. Since sewage sludge is an heterogenous mixture, a possible source of these organic acids could be from waste cooking oils or cell membranes pumped down the drain. Likely feasible routes to upgrade biocrudes with heavy nitrogen footprints have been suggested to be deamination, dehydroxylation and decarboxylation [26].

Table 3.4 Chemical composition data of HTL biocrudes from 300ºC using GC-MS

Categories	**Relative peak areas (%) recorded by GC-MS**					
Alkanes	**300 PD**	**300 Ca PD**	**300 Sec**	**300 Ca Sec**	**300 Tk**	**300 Ca Tk**
Cyclopentadecane	1.03	0.75		0.08		0.10
Tetradecane	0.61	0.56	0.26	0.22	0.13	0.14
Pentadecane	0.28	0.75		0.20		
3Trifluoroacetoxypentadecane			0.92	1.04	1.51	0.47
Other Alkanes	2.95	3.35	2.89	7.23	5.13	4.54
Sub-total	4.87	5.41	4.07	8.77	6.77	5.25
Alkenes						
1-Hexadecene	1.42	1.15	0.92	1.07	0.58	0.59
1-Pentadecene	1.01	1.38	0.87	1.09	1.26	
1-Tridecene	0.91	1.73	1.18	1.26		1.02
1-Nonadecene	0.61	0.52	0.88	0.52	0.70	0.76
Other Alkenes	3.94	5.87	4.07	3.73	3.35	2.67
Sub-total	7.89	10.65	7.92	7.67	5.89	5.04
Alkynes						
4-Octyne	0.16	0.07	0.37			
6-Methyl-3-heptyne		0.23			0.12	0.20
3-Heptyne		0.02	0.07	0.05	0.13	0.09
Other Alkynes	0.18	0.11		0.04	0.04	0.51

Sub-total	0.34	0.43	0.44	0.09	0.29	0.80
Aromatics						
Styrene	0.06	0.08	0.07			
Ethylbenzene	0.04		0.19	0.23		
Acenaphthene-d10		0.21			0.33	0.35
Phenol	0.71	0.77	1.18	1.41		0.28
Other Aromatics	24.17	24.12	21.51	21.60	21.01	19.77
Sub-total	24.98	25.18	22.95	23.24	21.34	20.40
N-compounds						
1-Adamantanamine, N,N-dimethyl-	1.33	0.28	1.00	1.27		
Hydrazine, (2,5-dichlorophenyl)-		0.13	0.12		1.10	0.24
Cyclohexanamine, N-cyclodecylidene-	0.41	0.21	0.36	0.47	0.11	0.33
3-Aminopyridine	0.08	0.08	0.07	0.13	0.05	0.10
Borazine, 2,4-dimethyl-			0.07		0.12	0.18
Other N-compounds	5.84	8.26	10.38	10.56	10.32	10.57
Sub-total	7.66	8.96	12.00	12.43	11.70	11.42
O-compounds						
9-Octadecenoic acid, (E)-	4.82	3.73	1.92	2.91	0.78	1.54
Octadec-9-enoic acid	3.60	3.85	2.59	1.46		
Oleic Acid	1.47	1.01	0.08	0.16	1.33	2.16

Ethanol, 2-(2,4-dichlorophenoxy)-	0.23	0.33	0.40	0.29	0.39	0.42
Dichloroacetaldehyde	0.03	0.04	0.04			0.07
Bromoacetic acid, hexadecyl ester			0.04		0.57	0.07
Other O-compounds	20.43	15.84	28.35	28.51	30.20	30.15
Sub-total	30.58	24.80	33.42	33.33	33.27	34.41
N-O compounds						
7-Tridecanone, oxime	0.99	0.52		0.90		
2-Butanamine, N-(2-furanylmethylene)-	0.12	0.23			2.50	2.52
Cyclopentadecanone, oxime	0.38	0.41	0.22	0.33	0.10	0.13
Other N-O compounds	16.01	18.49	10.58	10.88	10.48	10.50
Sub-total	17.50	19.65	10.80	12.11	13.08	13.15
Total detected area (%)	**99.20**	**99.17**	**99.31**	**99.27**	**94.73**	**94.35**

Figures 3.7 and 3.8 present the boiling point distribution obtained from the simulative distillation of HTL biocrudes at 300°C and 325°C respectively. The heavy diesel fraction (321°C-425°C) was the highest in all biocrude samples, thus corresponding with previous sludge study [36]

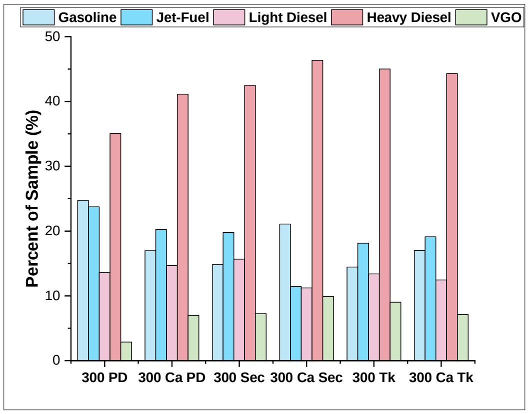

Figure 3.7 Sim distillation of 300ºC HTL biocrudes

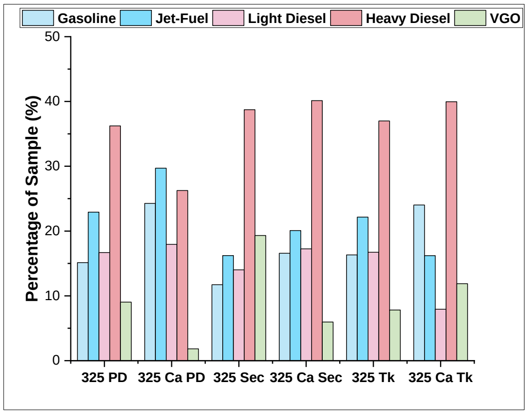

Figure 3.8 Sim distillation of 325ºC HTL biocrudes

Biocrudes from the liquefaction of pre-dried sludge had the highest light fraction (<193°C) of all the samples at 300°C and this slightly reduced at 325°C due to the production of heavy vacuum gas oil fractions. The increase in temperature from 300°C to 325°C can be seen to increase the vacuum gas fraction of the biocrude from pre dried sludge (from 2.9% to 9.0%) while the gasoline fraction reduced during this temperature (from 24.7% to 15.1%). This signifies that some of the light molecules were recombined to form larger molecules at higher temperature. On the integration of red clay to the liquefaction study using pre dried sludge, a new trend was observed. While the red clay favored more production of heavy diesel and vacuum gas fractions at 300°C, these fractions were reduced at 325°C in which lighter fuel fractions were formed. A reason for this might be a shift in the pH of the medium to alkaline conditions, which has been reported to favor the production of reduced heavy fractions [37]. A similar trend can be observed in the biocrude produced from secondary sludge.

The biocrude from the thickened sludge presented a slightly different trend from what was observed in the earlier discussed biocrudes. This suggests that higher temperature seemed to favor further decomposition of sugars to cyclic oxygenated compounds. Evidence of increased oxygenate formation can also be seen in the elemental oxygen composition of these biocrudes, which increased with increasing temperature.

3.4.4 Aqueous phase characterization

Figures 3.9 and 3.10 show the inorganic species content measured from the ion chromatographic study of aqueous phases derived from respective experimental processes. These ionic concentrations were higher than those reported from HTL aqueous phases at 350°C [38], thereby suggesting a precipitation of more ions into aqueous solutions at higher temperatures. High concentrations of potassium, sulfates, chlorides and phosphates were recorded in all the experimental aqueous phase products. This therefore provides a unique opportunity to recover nutrients that can be used for growing important energy feedstocks such as algae. The catalyzed aqueous phase products showed similar properties to the uncatalyzed reactions, expect for phosphate levels which generally reduced in red clay catalyzed reactions.

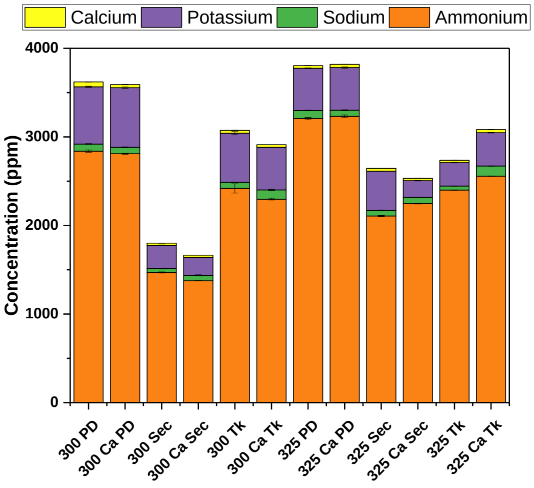

Figure 3.9 Cationic fractions in aqueous phases

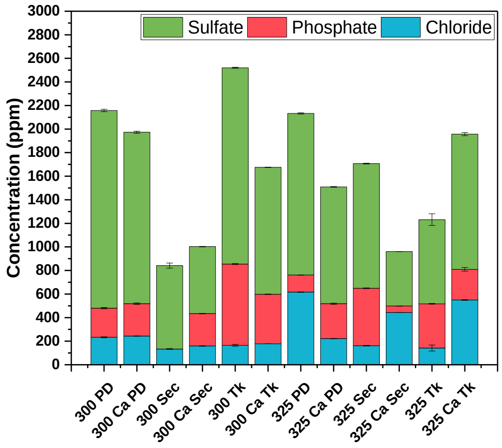

Figure 3.10 Anionic fractions in aqueous phases

The high levels of potassium and phosphates present an opportunity to recycle these valuable nutrients which can be used in the cultivation of photosynthetic biomass such as algae [39]. The aqueous phases derived from the HTL of pre dried sludge samples resulted in a higher concentration of both ions, indicating that the drying of wastewater solid feedstocks prevents the possibility of these nutrients to other product phases. Before wastewater streams for this process can be suitable for resource recovery, some concerns as regards concentration levels of ions need to be addressed. Although no direct link between calcium ion concentration and algal biomass yield has been found, evidences of increased phosphorus metabolism have been documented [40]. There is however a need to optimize the concentration of calcium ions in water streams intended for the algae, as excess amounts has been found to reduce the effectiveness of algal removal [41]. The sodium ion content of the HTL aqueous phases in this study generally ranged from 45.9 mg/L in the secondary sludge liquefied at 300ºC to 113.6 mg/L observed in the catalyzed thickened sludge at 325°C, which is above the threshold value set by the EPA[42]. Discharge of these water streams without sodium removal can lead to adverse situations such as eutrophication, water depletion and subsequently fish mortality. This concentration level however favors the growth of heterocystous blue-green algae, as it has been found not to inhibit photosynthetic carbon fixation [43]. The chloride ion concentrations of the aqueous species were considerably higher at 325°C, with a high of 616.4 mg/L detected in the pre-dried sludge product. A similar trend was noticed for the sulfate ion concentration, posing serious challenges to any constructive use of the wastewater as is. Possible solutions could be the removal of sulfate ions using an autotrophic bicathode [44] and ultraviolet disinfection in the case of chlorine.

3.4.4.1 Effect of red clay on aqueous phase quality

There was a general decrease in the total organic carbon (TOC) carbon content in the aqueous products with increasing temperature, and a similar trend has been previously reported [26]. This decrease signifies a reduction in the organic matter fractionated to the aqueous phase at higher products.

The total nitrogen (TN) composition in the aqueous phase derived from liquefaction experiments have been found from previous experiments to comprise of organic nitrogen, ammonium nitrogen, nitrite nitrogen and nitrate nitrogen [27]. In this study however, the major contribution to the total nitrogen was from the organic and ammonium nitrogen as the ionic nitrogen contents were below the detection level of the dionex ion chromatography instrument. From Table 3.6 below, the total nitrogen content and the ammonium nitrogen fraction can be found to slightly increase on increasing temperature, consequently leading to a decrease in the organic nitrogen content as verified by the aqueous phase yield (Fig 3.4). The aqueous phase from the catalytic runs followed the same trend, although their total nitrogen levels were lower than the uncatalyzed experiments as a result of nitrogen transformation to other phases [45].

The increase in temperature and the use of red clay as a catalyst did not significantly affect the pH of the aqueous phase products, as they are all slightly basic. The reduction in the organic content in the aqueous phase product can be further verified from the chemical oxygen demand (COD). The effect of temperature on the COD was more pronounced in the aqueous phase samples from the secondary sludge, as it reduced by 21.6% on increase in temperature from 300°C to 325°C. The pre-dried sludge aqueous product registered just a slight reduction (7.2%) in COD on liquefaction at 325°C, while the thickened sludge aqueous phase COD reduction was 16.6%. If the aqueous phase was to be treated using advanced oxidation processes therefore, the secondary aqueous phase products would be easily converted due to lower oxygen requirements.

Table 3.5 Other measured properties of HTL aqueous phases

Samples	**pH**	**COD (g/L)**	**TN (g/L)**	**NH4-N/TN (%)**
300 PD	8.7	89.7^{a}±0.4	9.6^{a,b,c}±0.9	29.5
300 Ca PD	8.6	85.9^{b}±0.7	9.8^{a,b}±0.6	28.6
300 Sec	8.5	59.9^{h}±0.2	3.3^{f}±0.4	45.1
300 Ca Sec	8.3	53.4^{i}±0.5	3.1^{f}±0.4	44.7
300 Tk	8.0	77.4^{d}±0.4	8.5^{b,c,d}±0.3	28.4
300 Ca Tk	8.2	73.1^{e}±0.2	7.9^{d}±0.5	29.0
325 PD	9.0	83.7^{c}±0.3	10.4^{a}±0.3	30.9
325 Ca PD	8.5	83.3^{c}±0.3	10.2^{a}±0.1	31.7
325 Sec	8.6	47.0^{j}±0.3	4.5^{e,f}±0.1	46.7
325 Ca Sec	8.4	43.3^{k}±0.1	5.3^{e}±0.0	42.2
325 Tk	8.2	64.5^{f}±0.2	7.6^{d}±0.7	31.4
325 Ca Tk	8.5	61.6^{g}±0.7	8.2^{c,d}±0.8	31.3

Different alphabets in the superscript of each column denote that the values are significantly different for each sludge type. Values after ± denote standard deviation.

3.4.4.2 Effect of red clay on aqueous compositional characteristics

Tables 3.7 and 3.8 show the common compounds found in the aqueous phases and their relative peak areas. All phases depicted the presence of many organic compounds as can be seen from the total areas detected (93.0% to 99.1%). The presence of acidic, hydrocarbon and nitrogen compounds in high concentrations presents an opportunity for aqueous phase recycling. Research studies in this regard that have been carried out found phenols, fatty acids, and nickel to be algal growth inhibitors [25]. The presence of these compounds in aqueous phases below means that dilution is necessary in order to guarantee optimum growth of selected plant species.

Table 3.6 Common detected compounds in the GC-MS analysis of HTL aqueous phases at 300ºC

No	RT	Compound	Peak Areas (%)						Molecular
			300 PD	300 Ca PD	300 Sec	300 Ca Sec	300 Tk	300 Ca Tk	Formula
1	12.7	1-Pentene, 2-methyl-	0.47	0.19	2.21	2.01	1.59	2.21	C_6H_{12}
2	16.7	2 – Propenal	1.06	0.53	3.19	2.43	0.61	1.86	C_3H_4O
3	21.3	Urea		1.27	0.45	0.36	0.68	1.44	CH_4N_2O
4	21.4	Aminocyanocetic Acid	2.40	0.74	2.74	2.48	2.48	2.05	$C_3H_4N_2O_2$
5	25.7	Pentanal	3.01	1.32	1.20	0.78	1.64	1.82	$C_5H_{10}O$
6	34.1	Acetaldehyde	2.14	0.80	1.15	0.39	0.04	0.26	C_2H_4O
7	36.7	Nitrous Oxide	7.64	23.28	18.86	25.85	18.95	24.27	N_2O
8	47.5	N-(2-Acetylcyclopentylidene) cyclohexylamine	5.24		2.94	4.58	3.62	3.81	$C_{13}H_{21}NO$
9	49.6	Cyclohexane-1,3-dione, 2-allylaminomethylene-5,5-dimethyl-		0.51	0.73	0.76	1.75	3.50	$C_{12}H_{17}NO_2$
10	50.7	1,1,3,3-Tetraallyl-1,3 disilacyclobutane	7.11	2.15	5.17	5.52	3.97	3.34	$C_{14}H_{24}Si_2$
11	52.4	Dodecahydropyrido[1,2-b] isoquinolin-6-one	3.12	8.99	0.49	5.69	9.39	7.84	$C_{13}H_{21}NO$

12	55.2	Propanamide	2.58	6.81	1.14	1.32	2.40	5.98	C_3H_7NO

The use of red clay as a catalyst did not generally alter the compositional characteristics of the aqueous phases, as most compounds could be traced across all the liquefied samples. There was, however, a decrease in the relative areas of the major compounds in the pre-dried and secondary sludge samples, while an increase in the relative areas of these compounds was observed in thickened sludge aqueous products. This trend was noticeable in compounds such as [RT: 12.67, 1-Pentene, 2-methyl-; RT: 16.67, 2-Propenal; RT: 21.4, Aminocyanocetic Acid; RT: 34.06, Acetaldehyde] at 300ºC, while areas in the thickened sludge samples increased for those compounds. Nitrous oxide was noticeable in large concentrations at 300ºC across all samples, but this decreased on increasing temperature. This suggests that these aqueous phases need to undergo further treatments before discharge into open waters can be possible. The compositions of these aqueous samples are very similar to the composition of their biocrude counterparts, and this was also confirmed from literature [28].

Table 3.7 Common detected compounds in the GC-MS analysis of HTL aqueous phases at 325ºC

No	RT	Compound	Peak Areas (%)						Molecular
			325 PD	325 Ca PD	325 Sec	325 Ca Sec	325 Tk	325 Ca Tk	Formula
1	10.37	3-Butenamide	0.76	2.93	1.42	0.45	0.85	1.34	C_4H_7NO
2	10.45	Aziridine, 2-methyl-	0.53	1.11	0.57	0.44	0.64	0.56	C_3H_7N
3	12.45	Methane, isocyanato-	0.44	0.08	1.16	1.36	0.49	0.92	CH_3NCO
4	16.44	Borane carbonyl	0.08	0.25	0.43	0.79	0.67	0.76	CH_3BO
5	25.32	Pentanal	0.57	3.70	1.24	0.28	2.78	2.13	$C_5H_{10}O$
6	26.52	Urea	0.37	0.91	0.61	0.41	5.03	4.28	CH_4N_2O

7	36.87	Nitrous Oxide	11.86	21.33	19.59	1.32	10.97	15.22	N_2O
8	39.37	Acetaldehyde	2.09	1.49	4.45	3.49	2.13	2.70	C_2H_4O
9	48.72	3-(Prop-2-enoyloxy)tetradecane				3.54	1.82	1.09	$C_{17}H_{32}O_2$
10	49.23	1-(2 Adamantylidene)semicarbazide			4.09	2.54	2.90	1.93	$C_{11}H_{17}NO$
11	55.81	Propanamide	5.99	2.37	0.70	1.41	3.99	0.92	C_3H_7NO
12	54.14	Propanamide, N-(aminocarbonyl)-	1.43	0.54	1.61	2.93	1.91	1.01	$C_4H_8N_2O_2$

3.4.5 Gas phase characterization

The micro GC analysis of gaseous products from the different liquefaction experiments showed the presence of CO_2, CO, H_2, CH_4 and the presence of C_{2+} gaseous compounds in trace amounts (Fig 3.12). The calculations were based on a nitrogen-free basis, as nitrogen was used to pre-pressurize the reactant mixtures at the start of experiments due to its non-oxidation and higher heating value improvement effects [46]. Because of this, CO_2 consisted of more than 90% of the gases formed in all experiments. In addition, the high amounts of CO_2 can be due to hydrothermal reactions favoring decarboxylation and water gas shift reactions (in which more H_2 might be consumed)- see chemical reactions 1 and 2 below. There was also a noticeable production of higher molecular weight carbon gaseous species such as propane, propene, and isobutene.

$$\text{Decarboxylation: } R \leftrightarrow R_1 + CO_2 \tag{1}$$

$$\text{Water gas shift reaction: } H_2O + CO \leftrightarrow H_2 + CO_2 \tag{2}$$

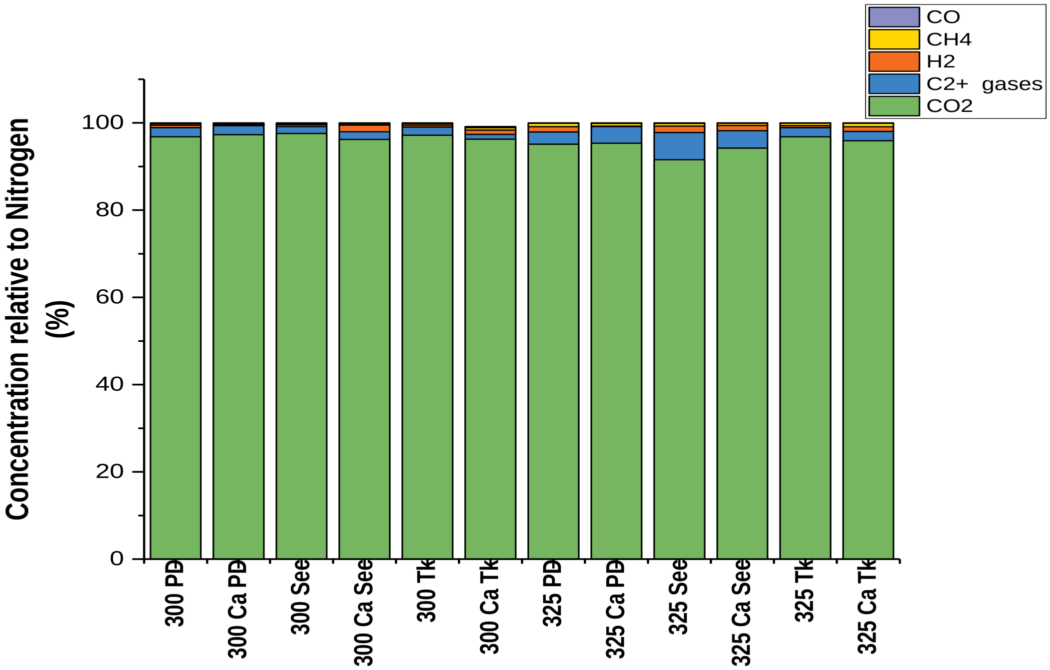

Figure 3.11 Relative area percentages of HTL gas components

The composition of the gaseous products in the catalyzed reactions did not vary much from experiments in which raw samples were used, although an increase in CO_2 was noticed in secondary sludge gas phase at 325°C. Gas scrubbing using desiccants such as iron sponges is needed prior to the use of this gas stream, as hydrogen sulfide concentrations have been reported [5].

3.4.6 Biochar characterization

The char derived from the hydrothermal liquefaction of sludge samples at respective temperatures was characterized using ash content, HHV and elemental analysis and listed in Table 3.9 below. The considerably low C and H content in the char samples resulted in a low HHV ranging from 5MJ/kg to 10MJ/kg. On comparison of the elemental components of produced chars with that of the sludge feedstocks (Table 3.3), the C, H, N and O contents significantly reduced in the char products. A possible explanation for this would be the removal and redistribution of C, H, N and O organics into the formation of biocrude, gaseous and aqueous fractions at elevated liquefaction temperatures [27]. The red clay catalyzed reactions resulted in a further reduction in the measured elemental yields in the biochars of all samples, and this effect can be seen mostly in C and N elemental compositions. This supports the tendency of red clay to favor the production of more C and N based compounds as observed in other liquefaction phases.

There was an increase in the ash contents of biochars from the red clay catalyzed reactions, signifying an increase in the metallic components retained in the biochars. Prior studies have reported a distribution of up to 90% of heavy metallic components in HTL chars, with increasing concentration levels at higher temperatures [13]. The increased ash contents in catalyzed experiments can thus be deduced to be as a result of heavy metal constituents present in the red clay used in this study, which has a high intensity of silica (Figure 3.2. Biochars with heavy metallic contents are being studied for possible applications in the production of sewage sludge activated carbons, due to their metal distributing abilities [17].

Table 3.8 Proximate and elemental analysis of HTL biochar products

Samples	**Ash; wt.%**	**HHV; MJ/kg**	**Elemental Analysis; wt. %**				
			C	H	N	S	O
300 PD	$63.9^{g}\pm0.5$	$8.4^{b}\pm0.3$	$24.9^{a} \pm 0.12$	2.8 ± 0.02	$2.8^{a} \pm0.02$	0.5 ± 0.03	$5.4^{a,b} \pm0.14$
300 Ca PD	$75.2^{d}\pm0.3$	$6.6^{d}\pm0.3$	$15.7^{c,d} \pm0.04$	2.1 ± 0.06	$1.9^{c,d} \pm0.01$	0.5 ± 0.04	$4.6^{b} \pm0.07$
300 Sec	$57.1^{i}\pm0.5$	$8.7^{b}\pm0.2$	$14.8^{d,e} \pm0.21$	1.9 ± 0.05	$1.9^{d} \pm0.03$	0.4 ± 0.03	$4.4^{b} \pm0.46$
300 Ca Sec	$76.9^{c}\pm0.2$	$6.6^{d}\pm0.1$	$9.6^{g} \pm0.36$	1.4 ± 0.04	$0.9^{i} \pm0.04$	0.3 ± 0.02	$4.9^{a,b} \pm0.26$
300 Tk	$61.9^{h}\pm0.6$	$9.5^{a}\pm0.3$	$26.8^{a} \pm0.16$	2.9 ± 0.05	$2.8^{a} \pm0.01$	0.6 ± 0.03	$5.6^{a,b} \pm0.24$
300 Ca Tk	$75.9^{c,d}\pm0.1$	$5.8^{e}\pm0.3$	$15.0^{d} \pm 0.91$	2.0 ± 0.10	$1.7^{e,f} \pm0.08$	0.3 ± 0.02	$5.1^{a,b} \pm1.11$
325 PD	$67.8^{f}\pm0.1$	$8.3^{b}\pm0.1$	$21.0^{b} \pm 0.01$	2.3 ± 0.16	$2.4^{b} \pm0.03$	0.5 ± 0.00	$6.2^{a,b} \pm0.20$
325 Ca PD	$79.1^{b}\pm0.2$	$5.8^{e}\pm0.2$	$13.7^{d,e,f}\pm0.15$	1.8 ± 0.06	$1.4^{g} \pm0.05$	0.4 ± 0.02	$3.5^{b} \pm0.28$
325 Sec	$67.7^{f}\pm0.2$	$10.0^{a}\pm0.1$	$16.8^{c,d} \pm0.16$	2.0 ± 0.09	$2.1^{c} \pm0.04$	0.7 ± 0.04	$5.6^{a,b} \pm0.29$
325 Ca Sec	$81.0^{a}\pm0.2$	$6.1^{d,e}\pm0.1$	$11.1^{e,f,g}\pm0.14$	2.3 ± 0.86	$1.6^{f,g} \pm0.01$	0.4 ± 0.05	$4.7^{b} \pm0.91$
325 Tk	$73.6^{e}\pm1.2$	$7.3^{c}\pm0.1$	$19.2^{b,c} \pm2.56$	2.2 ± 0.24	$1.8^{d,e} \pm0.11$	0.5 ± 0.01	$8.9^{a} \pm2.44$
325 Ca Tk	$79.9^{a,b}\pm0.3$	$5.1^{f}\pm0.1$	$11.1^{f,g} \pm1.45$	1.9 ± 0.25	$1.1^{h} \pm0.03$	0.5 ± 0.05	$4.7^{b} \pm1.48$

Different alphabets in the superscript of each column denote that the values are significantly different for each sludge type. Values after ± denote standard deviation.

3.5 Conclusions

Hydrothermal liquefaction was carried out on three different types of sludge samples having different solids content. The highest biocrude yield (37.7±1.6 wt. %) was obtained from the thickened sludge (15% solids content) liquefied at 325ºC, while the lowest biocrude yield (21.5±1.3 wt. %) was obtained from the secondary sludge (5% solids content) liquefied at 300ºC. Red clay catalyzed reactions reported slightly lower biocrude yields and heating values but there were significant improvement in the moisture content (4.4±0.3% to 1.0±0.1% in the pre-dried sludge liquefied at 300ºC), Total Acid Number (18.6±0.4 mgKOH/g to 15.7±0.2 mg KOH/g in the thickened sludge liquefied at 325ºC) and kinematic viscosity (48.8 cSt to 14.5 cSt in the secondary sludge liquefied at 300ºC). The highest biochar yield (16.0±0.1 wt. %) for the uncatalyzed experiments was recorded in the secondary sludge liquefied at 325ºC, while the lowest yield

(9.7±1.5 wt. %) was obtained in the thickened sludge liquefied at 325ºC.In all experiments, the catalyzed runs resulted in an increase in the biochar yield possibly due to the heavy metallic components in the red clay as verified by XRD analysis. Considerably low biochar heating value (5 to 10 MJ/kg) was recorded, but this can find use in the production of sludge based activated carbon owing to its high metallic imprint.

The aqueous fractions derived from all experiments were slightly alkaline and heavily polluted with nutrients. The use of red clay as a catalyst resulted in slight reduction in the TOC, COD and TN. Slight reduction in the cationic and anionic constituents in the aqueous phase was recorded in the catalyzed runs (sulfate ion reduction from 708mg/L to 585.5mg/L in the aqueous phase derived from liquefying secondary sludge at 300ºC), but far more nutrient recycling is necessary for this effluent water to meet regulatory requirements. The gaseous fraction increased on increasing temperature and a maximum yield of 28.8±0.1 wt. % was obtained in the pre-dried sludge liquefied at 325ºC, with a low of 12.9±0.1 wt.% obtained in the secondary sludge liquefied at 300ºC. The integration of red clay catalyst slightly reduced the gaseous phase yields, but the overall composition was like the uncatalyzed runs. The major component remained CO_2, and this could find use in steam generation processes after removal of some poisonous constituents such as sulfides.

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Chapter 4

Catalytic upgrading of bio-oil produced from the hydrothermal liquefaction of municipal sludge

4.1 Abstract

Catalytic upgrading of municipal sludge based biocrudes became necessary due to high amount of heteroatoms (N,S and O) present in the oil. The cost of catalysts could significantly impact the economics of the overall cost of the fuels, and research into low cost catalytic options became necessary. Triglycerides such as waste cooking oil and non-edible oils have been studied for possible reintegration as liquid transportation fuels. Catalytic cracking of these triglycerides helps to break the glyceride backbones, thereby producing fuels with improved viscosity and higher heating value. The synergistic effect of hydrotreating this cracked carinata oil with sludge biocrude over inexpensive Ni/SiO_2-Al_2O_3 is explored in this study.

The catalytic upgraded oil yields at 250°C 3h, 300°C 1h, 350°C 1h and 350°C 30min did not vary significantly, although longer processing times favored the production of more solids. The higher heating value of the produced liquids was also comparable to petroleum-based liquid fuels (highest value of 45.1±0.6 MJ/kg was obtained when processing was at 350ºC for an hour. The 350°C 30min processing condition produced the highest liquid (61.0±1.3 wt.%) and lowest solid (12.5±2.54 wt.%) fraction, and was comparable to the production distribution from 300°C obtained at 1hour processing time. However due to an improvement in the total acid number (3.3±0.1 mg KOH/g) and kinematic viscosity (6.3±0.2 CSt) compared to the product obtained from 300°C and 1hour (which were 7.4±0.4 mg KOH/g and 13.0±1.9 CSt respectively), the 350°C 30min processing time was selected for further study. Increase in the catalyst loading rate from 2.5wt.% to 5wt.% resulted in the production of liquid fractions with improved viscosity and

acidity, and the production of higher carbon gases due to further cracking of heavier compounds. The use of uncracked (raw) carinata oil as opposed to cracked carinata oil resulted in significantly lower liquid yield with lesser hydrogen consumption, suggesting slower levels of hydrodeoxygenation. The liquid, however, had a significantly lower total acid number of 0.89±0.07 mg KOH/g. The use of the model erucic acid also resulted in further lower liquid yield and markedly high amounts of higher carbon species in the gas phase.

4.2 Introduction

Energy is fundamental to how the transportation sector operates. Currently, about 94% of the energy required by the transportation sector is from fossil-based fuels. It has been estimated that renewable energy resources can reduce transportation sector fossil fuel need to 85% by 2040[1]. Since a significant portion of the reduction in the use of petroleum oil in the transportation sector will be due to increase in production of biofuels, there is therefore an urgent need to address the cold flow properties, stability, acidity and heteroatomicity challenges that has limited the integration of more biofuels in the transportation sector.

Sewage sludge is a byproduct of wastewater treatment processes, and is typically an agglomeration of organics, metals and pathogens [2]. Traditional sludge treatment processes such as landfilling and composting have faltered in providing an environmentally friendly approach to the treatment of these wastes, mostly because of their large processing volume, waste sorting challenges and emission of toxic contaminants [3-4].

Hydrothermal processing is the thermochemical conversion of wet biomass feedstocks (typically in slurry form) at elevated conditions of temperature and pressure, resulting in products with somewhat simple chemical structures [5]. Hydrothermal liquefaction (HTL) is a form of hydrothermal processing well suited for the conversion of waste streams such as sewage, due to its ability to process feedstock in wet form [6]. Furthermore, HTL has been found to be versatile in the conversion of various sewage sludge types and in the dechlorination and removal of emerging contaminants [7-11]. Spectroscopic assessment of the biocrude fraction of HTL products has revealed the presence of structurally diverse oxygenated compounds from those contained in petroleum, although with much similarity to crudes from algal biomass [12-14].

Apart from the structural dissimilarity with petroleum crude oil, biocrude from HTL of sewage sludge contains heteroatoms such as 2 – 7% nitrogenates [15-16] and 2 – 19% oxygenates [17-18], and has about 80% of the higher heating value of petroleum crude. The presence of these heteroatoms in the biocrude results in thermal unstability, high corrosion and release of poisonous substances (SOx and NOx) on combustion. Further upgrading of these biocrudes is therefore a necessity if usage as transportation fuels is a goal.

Upgrading (or hydroprocessing) are catalytic processes that address the heteroatomic challenges in biocrudes through hydrocarbon saturation and hydrogenolysis [19]. It is the largest application of industrial catalysis, and the degree of success typically depends on the nature of the catalyst being used and the operating conditions. Hydrotreating is the most widely used upgrading process in the petroleum industry, and it entails improving the quality of liquid fuels without much alteration to the boiling point range of the respective fractions [20]. This technology has been widely deployed into the treatment of biocrudes but is typically tuned to suit the heteroatom of concern i.e. sulfur removal (HDS), oxygen removal (HDO) and nitrogen removal (HDN). Oxygen removal (HDO) is one of the major biocrude upgrading steps due to its ability to improve volatility, thermal stability, and reduce viscosity of biocrude [19]. Catalytic HDO is preferred over thermal HDO due to its increased reaction rate, and can be carried out at mild (250°C) or at severe (350°C) temperatures. Conventional CoMoS and NiMoS catalysts that were evaluated for the upgrading of sludge biocrude; produced high quality fuels with 1 wt.% O , <0.05 wt.% S, <0.01mg KOH/g acidity and 2.7Cst viscosity at 20°C [17]. A major challenge that has been reported, however, is the manner of catalyst preparation (pre-sulfidation), and the leaching of sulfur into the produced oils [21].

Cracking (or catalytic pyrolysis) is another conventional refinery technology that is now applied to the further processing of biomass oils because of the following advantages: lower temperature and pressure requirements, lack of water in the product phase, and eliminating the need for hydrogen. It has interesting advantages such as lower temperature and pressure requirement, lack of water in the product phase and canceling the need for hydrogen. However, cracking promotes catalyst deactivation and the formation of coke, thus leading to a lower quality oil when compared to oil from hydrotreating. The lower quality is a result of the targeted disruption of C–C and C–O bonds, thus favoring ring opening reactions [19].

Production of biofuels from non-edible food crops and waste triglycerides is being given a lot of consideration to reduce the impact of biofuel production on food crops. Waste triglycerides (such as waste cooking oil, waste fish oil and waste oil from saponification processes) are highly viscous and moderate heating value oils that have potential in the production of liquid transportation fuels. Diesel range (C_{16} – C_{18}) fuels obtained from hydrotreating of waste oils provide almost no challenges when co-processed with crude oil [22-23]. Catalysts are vital in these studies, as they help to remove heteroatoms in the oils and also maintain thermal equilibrium. Alcohols, aldehydes, and alkanes were also produced as hydrotreating intermediates. However, the development of environmentally friendly and highly selective catalysts remains a challenge [24-25]. The catalytic cracking of jatropha oil (non-edible vegetable oil) at 375°C with a composite mixture of ZSM-5 and SiAl catalysts produced fuels which had 36% gasoline (C7-C11) and 58%

diesel (C_{12}-C_{22}) [26]. When camelina oil was cracked with 20% wt.% Zn doping on ZSM-5, a 2-fold hydrocarbon yield of 77.5% was obtained when compared without catalyst use [27].

Brassica Carinata species an oleaginous, is one of the oldest cultivated oil crops in Ethiopia. Favorable characteristics of *B.carinata* compared to other oilseeds include higher oil yield and quality, higher hot and cold weather tolerance, and lower input requirements such as fertilizers and water [28]. These qualities enable the sustainable growth of *B.carinata* in harsh growing conditions such as clay- or sandy-soils and semi-arid temperature regimes. It is at the crossroads in the food versus energy debate however, as it can be processed into edible oil and/or industrial oil. *B.carinata* is however used for industrial applications because of the high concentration of erucic acid and associated toxic effect on the heart when ingested at high concentrations [29].

The effect of fresh and regenerated Zn/Na-ZSM-5 on the cracking of *B.carinata* oil revealed a 35% increase in hydrocarbon yield when the catalyst was reused, with lesser coke and distillation residual [30]. This is a significant finding due to reservations about the hydroprocessing of oils, due to the increased hydrogen cost. Hydroprocessing of *B.carinata* over Mo-Zn/Al_2O_3 catalyst has also reported an improvement in qualities such as hydrocarbon content, moisture, density, TAN and HHV while preserving the crystalline nature of the Al_2O_3 support [31]. Higher hydrotreating temperatures however led to the production of more gaseous products, leading to a decrease in the liquid yield.

Co-processing of low heating-value fuels is being explored by researchers, because it provides an opportunity to co-treat two feedstocks without the need to construct new processing facilities thus improving the economics of the whole process. The selection of an effective catalyst however remains a challenge, as the catalyst needs to accommodate the characteristics of both feedstocks without compromising the quality of the produced fuel [32]. The co-processing of vacuum gas oil, waste lubricating and cooking oils over NiO-WO_3 at 400°C led to a general increase in the gasoline octane number with a decrease in diesel cetane index. The composition was however found to be affected by which feedstock components was in higher quantity [33].

Silica-alumina catalysts are versatile catalytic materials that have found increased relevance in a wide range of product synthesis (e.g. cracking, oligomerization, dehydration, and isomerization processes) [34]. These catalysts are solid acids with modifiable acid strength, with high degree of stability at temperature regimes up to 500-700°C, with exciting properties due to the combinative effects of amorphous silica and strong Lewis acid sites offered by the alumina support.

The influence on metal support on silica-alumina catalysts was studied in the HDO of transesterified karanja oil. Nickel loading of greater than 20 wt.% was found to result in high liquid (80%), with properties much comparable with light diesel oil [35]. Catalysts with high nickel loading (29 – 58 wt.%) have also proven effective in the hydrotreating of pyrolysis oils, producing fuels with lower oxygen content and increased higher heating values [36-37].

The studies from the hydrotreating of sewage based biocrudes and cracking of non-edible oils have been encouraging, although limited. There is, therefore, a need to study closely the synergistic effect of hydrotreating biocrudes and cracked oils in order to evaluate the heteroatom removal rate as well as the degree of hydrogen consumption. This study seeks to address this gap in literature, and specifically provide information on the:

1. Influence of hydrotreating temperature on the yield and quality of the upgrading product fractions from co-processing sewage sludge biocrude and cracked oil over Ni/SiO_2-Al_2O_3

2. Influence of optimum condition parameters such as catalyst loading, initial hydrogen pressure, use of uncracked oil and model fatty acid on the product quality.

4.3 Materials and methods

4.3.1 Feedstocks and reagents

Pre dried sludge (secondary thickened sludge but dried prior to use) was obtained from the H.C. Morgan Pollution Control Treatment plant located in Auburn, Alabama, USA. The sludge was dried at 105°C at 24h, blended and stored at 4ºC before experiments. The detailed characterization of the sludge has been reported in Chapter 3. The *Brassica Carinata* oil used in this study was obtained from Agrisoma Biosciences Inc., and the fatty acid profile was reported as: Myristic acid (C 14:0) – 0.1%, Palmitic acid (C 16:0) – 3.5%, Palmitoleic acid (C 16:1) – 3.0%, Stearic acid (C 18:0) – 1.2%, Oleic acid (C 18:1) – 10.8%, Linoleic acid (C 18:2) – 18.0%, Linoleic acid (C 18:3) – 13.6%, Arachidic acid (C 20:0) – 0.9%, Gadoleic acid (C 20:1) – 8.8%, Behenic acid (C 22:0) – 0.8%, Erucic acid (C 22:1) – 39.2% and Lignoceric acid (C 24:0) – 1.0%. The oil was extracted from the seed species using hexane, due to its low boiling point (50 – 70%) and superior extraction ability (up to 95% of oil in the seed). Commercial nickel on silica/alumina (~65 wt.% Ni loading) catalyst power obtained from Sigma-Aldrich (No. 208779,St. Louis, MO, USA) was used as received in the HDO experiments. High purity nitrogen and hydrogen (Airgas, PA, USA) were used for the cracking and HDO experiments.

4.3.2 Hydrothermal liquefaction (HTL) of sludge

HTL experiments were performed in a Parr Instrument Company high pressure reactor (model 4578). The reactor has a capacity of 1800 mL and is equipped with a controllable stirrer, PID controlled heating surface, pressure gauge and J-type thermocouple. HTL experiments were performed at 325ºC with a residence time of 60min and a continuous mixing of 95RPM. Details of the liquefaction product separation has been extensively discussed in the previous chapter (Chapter 3). The main feedstock of this upgrading study, the 325 pre dried sludge biocrude (called "HTL OIL" hereafter) was then stored at - 20ºC prior to use.

4.3.3 Catalytic cracking of hexane-extracted *Brassica Carinata* oil

The chemical cracking of the *Brassica Carinata* oil was carried out in a Parr Instrument Company high pressure reactor (model 4598) with a capacity of 100mL. For each cracking experiment, 50g of the oil and 1g of Ni/SiO_2 – Al_2O_3 were loaded into the reactor. The Ni catalyst was used as-received without any pre-treatment. The reactor was repeatedly purged with nitrogen to create an inert atmosphere. The reactor was then charged with 2.4MPa of the gas. On-stream gas analysis was done prior to and after the end of experiments using an INFICON Micro GC 3000, in order to measure accurately the compositional volume of gaseous products. Cracking was carried out at 400ºC, 1h residence time and a constant stirring speed of 600RPM. At the end of the reaction, the reactor was cooled to room temperature (~20°C) using both the internal cooling coil and an external air fan. The gas products were then analyzed prior to opening the reactor. After each experiment, the liquid products were collected in tubes and centrifuged to a g-force of 1240 Clay Adams (420089, Parsippany NJ) for 5mins. The resulting liquid (named CRK HEBCO) and solid (catalyst and coke) phases were then separated by decantation. The solid was only characterized for ultimate analysis (ASTM D5373 – 02; Elementar) while the cracked oil (CRK HEBCO) was used as the co-upgrading feedstock for the study.

4.3.4 Hydrodeoxygenation of HTL OIL and CRK HEBCO

The HTL OIL and CRK HEBCO were subjected to hydrodeoxygenation reactions using a 100mL batch reactor (Parr Instruments, Moline, IL, USA). Preliminary experiments were conducted with 1:1, 1:2 and 1:3 ratios of HTL Oil and CRK HEBCO. Highest amount of solids was produced from the 1:1 mix ratio while the 1:2 mix ratio produced the lowest amount of solids. The 1:2 mixture ratio was therefore selected for more study. The products from the other mixing ratios were not characterized beyond the yield measurements. In a typical test, a 1:2 liquid mixture of HTL OIL (6.6g) and CRK HEBCO (13.4g) were added to the catalyst (0.5g) to achieve oil to catalyst ratio of 40:1. The reactor was then purged with nitrogen and hydrogen, after which the reactor was pressurized with hydrogen (6.9MPa). Pre and post gas analyses were carried out using an INFICON Micro GC 3000 in order to determine the hydrogen consumption. The hydrogen consumption was calculated as follows [36]:

$$\text{Hydrogen consumption}\left(\frac{\text{mol H}_2}{\text{kg bio-oil}}\right)=\left[n_{i,\,\text{H}_2}-x_{f,\text{H}_2}\times n_{f,\,\text{total}}\right]\times\frac{1}{20g\ \text{bio-oil}}\times\frac{1000g}{1kg}\tag{1}$$

where $n_{i,\,\text{H}_2}$ = initial no of moles of hydrogen prior to upgrading
$x_{f,\,\text{H}_2}$ = final mole fraction of hydrogen in the gas product stream
$n_{f,\,\text{total}}$ = total no of moles of gas at the end of experiment

The liquid products were collected in tubes after each experiment, and centrifuged to a g-force of 1240 Clay Adams (420089, Parsippany NJ) for 5mins. Both the liquid and the solid (catalyst and coke) phases were then separated and weighed. The weight values were used for mass balance calculations. The total mass of gas produced was calculated as follows [37]:

$$\text{Weight of gas (g)} = \sum_i\left[x_i\times MW_i\times n_{\text{total}}\right]\tag{2}$$

where x_i = mole fraction the gas i
MW_i = molecular weight of the gas i (in g/mole)
n_{total} = total number of moles of gas product

The product yield of the respective phases (solid, gas and solid) were also calculated as:

$$\text{Oil yield} = \frac{W_L}{W_F} \times 100 \qquad (3)$$

$$\text{Gas yield} = \frac{W_G}{W_F} \times 100 \qquad (4)$$

$$\text{Solid yield} = \frac{(W_T - W_C)}{W_F} \times 100 \qquad (5)$$

Where W_F = mass of the co-upgrading feed (g)
W_L = mass of the liquid product (g)
W_G = mass of the gas product (g)
W_T = mass of the total solid residue (g)
W_C = mass of the catalyst (g)

To study the influence of the initial hydrogen pressure and the cracked oil co-feed, cracking experiments were carried out using the same methodology above. The only difference was an initial nitrogen pressure of 2.4MPa and the absence of catalyst in both cases. The summary of the experimental plan is presented below:

Table 4.1 Experimental design for feedstock co-upgrading

Feedstock	T and time	Catalyst loading	Atmosphere	Number of runs
HTL OIL+CRK HEBCO	250 3hr	2.5 wt. %	H_2	1
HTL OIL+CRK HEBCO	300 1hr	2.5 wt. %	H_2	1
HTL OIL+CRK HEBCO	350 1hr	2.5 wt. %	H_2	2
HTL OIL+CRK HEBCO	350 30min	2.5 wt. %	H_2	2
HTL OIL+CRK HEBCO	350 30min	No cat	H_2	2
HTL OIL+CRK HEBCO	350 30min	5 wt. %	H_2	2
HTL OIL+CRK HEBCO	350 30min	2.5 wt. %	N_2	1
HTL OIL+CRK HEBCO	350 30min	No cat	N_2	1

HTL OIL+UNCRACKED	350 30min	2.5 wt. %	H_2	1
HTL OIL+ERUCIC	350 30min	2.5 wt. %	H_2	1

4.3.5 Feedstocks and product characterization

4.3.5.1 Physical properties

The water content of the HTL oil, cracked *Carinata* oil, co-upgrading feed and products was determined using the Karl-Fischer titration on a V20 volumetric KF titrator from Mettler Toledo (ASTM D6869 method). Total acid number (TAN) in mg KOH/g of the feedstocks and products were determined with a Mettler Toledo T50 Titrator (ASTM D664-18e2 method). Density and kinematic viscosity of the feedstocks and products were measured at 40ºC using the Anton Paar Stabinger SVM 3000 (Ashland, VA, USA) viscometer.

4.3.5.2 Chemical properties

Elemental composition of the feedstocks, hydrotreated oil and solid products were determined on a vario MACRO cube from Elementar (Ronkonkoma, NY, USA) using the ASTM D5373 – 02 method. Higher heating value (HHV) measurements of the dried sludge and the solid hydrotreated products were determined using the Dulong's formula [38]:

$$\text{HHV (MJ/kg)} = 33.86 \times C + 144.4 \times (H - O/8) + 9.428 \times S \qquad (6)$$

The liquid feedstock and hydrotreated oil higher heating values were determined using correlation developed by Channiwala and Parikh [39]:

$$\text{HHV (MJ/kg)} = 34.91 \times C + 117.83 \times H - 10.34 \times O - 1.5 \times N + 10.05 \times S - 2.11 \times \text{Ash} \qquad (7)$$

Fourier transform infrared spectroscopy (FTIR) spectra within the wavelength range of 400 to 4000 nm were determined for the feedstocks and liquid hydrotreated products by applying ~20mg of sample on a Thermo Nicolet iS 10 (Thermo Scientific, Waltham MA) equipment.

4.3.5.3 Thermal properties

The thermal decomposition of the feedstocks, liquid and solid products was studied using a TGA-50 Shimadzu thermogravimetric analyzer (Columbia, MD, USA) with 20µL alumina crucible. About 10mg of sample was used for analysis, and was heated from room temperature to 650ºC at a heating rate of 10ºC/min and under nitrogen atmosphere (flow rate of 20ml/min).

4.3.5.4 Gas analysis

The compositions of the gaseous products were measured using an INFICON Model 3000 Micro Gas Chromatograph (GC) equipped with a thermal conductivity detector (TCD). The installed columns included Molsieve (30µm × 320µm × 10m), PLOTU backflush (30µm × 320µm × 3m), PLOTU fixed (30µm × 320µm × 6m) and a Variable OV1 (2µm × 150µm × 14m). Ultra-high purity helium (99.999%) was used as the carrier gas, and the measured gases included hydrogen, saturated and olefinic hydrocarbons (C_1–$C_5$and C_{6+} grouped peaks) and permanent gases (O_2, N_2, CO and CO_2).

4.3.6 Statistical analysis

Results were expressed as mean ± S.D. Differences between groups was analyzed using ANOVA and Tukey test using the SAS statistical software package (Version 9.4, SAS Institute Inc., Cary, NC) for windows. A p-value of less than 0.05 was considered to be statistically significant.

4.4 Results and discussion

4.4.1 Feedstock characterization

The pre-dried sludge ("PD" hereafter) used for the liquefaction had a higher heating value of 16.8±0.1 MJ/kg, and carbon, hydrogen, nitrogen, sulfur and oxygen contents of 38.9±0.1 wt.%, 5.4±0.1 wt.%, 6.4±0.0 wt.%, 0.2±0.1 wt.%, 23.1±0.1 wt.%, respectively. These values are similar to those obtained from other studies [40], although lower nitrogen and higher oxygen contents were reported by other researchers [41-42].

When HTL was applied to the sludge sample, the oil yield was 34.8±1.0 wt.% (d.b., ash free). The oil from the sample had a higher heating value of 32.0±0.6 MJ/kg, an acid content of 16.1±0.6 mg KOH/g and a nitrogen content of 6.0±0.7 wt.%. These values are also comparable to those obtained from similar feedstocks, although higher heating values and acid numbers were reported because of the higher temperatures used in these studies (340°C and 350°C respectively) [17,42]. The cracking of the B.carinata oil ("CRK HEBCO" hereafter) yielded 81.1±1.6 wt.% of a liquid phase, which was dark in color. The cracking process tremendously improved the nitrogen content (53.9% removal), oxygen content (89.2% removal) and kinematic viscosity (43.6 cSt to 15.8 cSt) of the non-edible oil, while the higher heating value also improved from 36.0±1.0 MJ/kg to 44.2±0.2 MJ/kg. The viscosity of the carinata feedstock was lower than a previously reported value [30]. This is possibly due to the method of extraction; reported values were extracted using cold press, while the carinata used in this study was extracted using the hexane solvent. The mixing of the cracked carinata with the HTL Oil ("Cracked HEBCO + HTL oil" hereafter) at the (2:1) mix ration resulted in a hydrotreating feed which benefited from properties of parent feedstocks; the HTL oil helped to slightly improve the acidity of the resulting mixture while the nitrogen and oxygen contents improved as well, as shown in Table 4.2. Further insights into this phenomenon can be explained by FTIR (Fig A4.1 in supplementary data). The cracking of the carinata oil resulted in the disappearance of the C-O and C-O-C stretching vibrations normally observed within 1200 to 800 cm^{-1}, while the CH_2 and CH_3 vibrations at 1500 to 1300cm^{-1} also reduced in intensity. This inferential ring opening properties provided by the cracking of the carinata oil were then transferred to the CRK HEBCO + HTL OIL mixture.

Table 4.2 Properties of the feedstocks used in this upgrading study

Properties	PD	HTL oil	CRK HEBCO	CRK HEBCO+HTL Oil
Composition (wt. %)				
N	6.4 ± 0.0	6.0±0.7	0.1±0.0	1.7±0.0
C	38.9± 0.1	66.1±0.4	85.5±0.7	80.1±2.9
H	5.4 ± 0.1	9.1±0.5	12.3±0.1	11.5±0.0
S	0.2 ± 0.1	0.7±0.0	0.1±0.1	0.3±0.1
O*	23.1 ±0.1	17.4±1.6	1.9±0.6	6.5±3.0
HHV (MJ/kg)	16.8 ±0.1	32.0±0.6	44.2±0.2	40.9±0.7
Water content (wt.%)	N.A.	2.8±1.0	B.D.L	B.D.L
TAN (mg KOH/g)	N.A.	16.1±0.6	79.4±0.0	56.1±0.8
Density (g/cm^3)	N.D.	1.1±0.0	0.9±0.0	1.0±0.1
Viscosity (mm^2/s)	N.A.	14.1±0.9	16.3±0.7	15.1±0.5

*Calculated by difference. Values after ± denote standard deviation. N.A: not applicable. N.D: not determined. B.D.L: below determination level.

4.4.2 Hydrotreating product yields and characterization

Figure 4.1 reveals the product yield from the co-upgrading of HTL oil and cracked carinata oil under four scenarios with Ni/SiO_2-Al_2O_3 catalyst loading of 2.5 wt.%. In all experiments, the reaction times shown was recorded after the programmed temperature was reached. The upgrading feed was converted into upgraded oil, gas and a solid residue. The total mass balance closure varied between 80.2 wt.% and 89.2 wt.%. The complete closure was not attainable due to reasons such as oil spillage during product retrieval and loss due to incomplete removal from the walls of the reaction vessel.

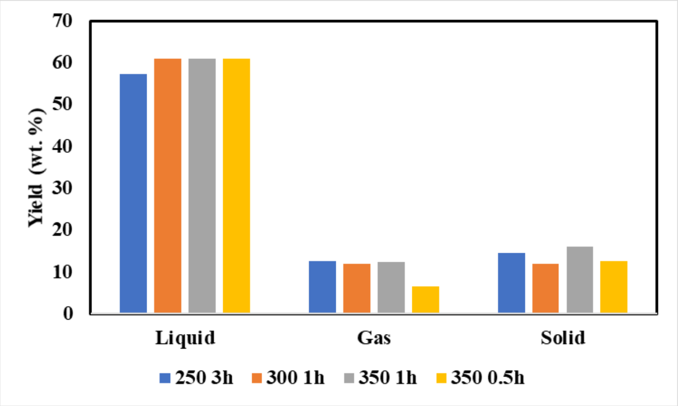

Figure 4.1 Product yields from the co-upgrading of HTL Oil and CRK HEBCO

The co-hydrotreatment of the HTL oil and the cracked non-edible oil was generally successful when compared with the hydrotreatment of the HTL oil alone. The hydrotreatment of the HTL oil alone led to the solidification of the product, possibly due to a rapid polymerization of the heavy compounds in the bio-oil (Fig 4.2). Furthermore, hydrotreating the HTL oil alone led to corrosion of the equipment and this is not favorable for HDO or catalyst activity. The use of common hydrotreating solvents such as butanol and tetrahydrofuran (THF) was also explored. Apart from the extremely low liquid yields (14.65 wt.% for butanol and 8.75 wt. % for THF), the liquids were of low quality. After a few hours after production, the liquid appeared to be polymerizing which could suggest that the heavier compounds in the bio-oil were not removed (Fig A4.2).

Figure 4.2 Product solidification and equipment corrosion during the upgrading of HTL oil alone

The highest oil yield of 61.0 wt.% was obtained during the conversion at 350°C and 30min, and was slightly higher than the lowest yield of 57.3 wt.% obtained by processing at 250°C and 3hours. All the liquid products were light brown in color. Processing the feedstock at slightly longer residence time (i.e. 350°C and 1hr) resulted in a slight reduction in the liquid yield (60.9 wt.%), and considerable amounts of gas (12.3 wt.%) and solids (16 wt.%) were formed. The same trend was noticed at lesser temperatures (250°C and 300°C), where longer hydrotreating residence times resulted in gas and solid yields of; 250°C - 12.7 wt.% and 14.5%, 300°C – 11.9 wt.% and 12 wt.% respectively. The observed yield at 350°C was comparable to a similar biocrude hydrotreated over CoMoS [17]. Co-upgrading did not also alter similar yield patterns that was observed in the cracking and hydrotreating study of waste cooking oil over alumina [43].

Hydrotreating temperature impacted the properties of the HDO liquid and gas products. Table 4.3 highlights the elemental properties and other observed properties of the liquid and gaseous products. Increasing the temperature slightly increased the hydrogen consumption from 44.9 mol/kg HTL oil to 45.4 mol/kg, suggesting an increased hydrodeoxygenation. Processing for longer residence times had significant effect on the rate of deoxygenation and denitrogenation, although the shorter times seems to favor desulfurization. The N content at longer times (250°C 3hr and 350°C 1hr) were 0.6 wt.% and 0.6 wt.%, corresponding to removal rates of 67.4% and 64.5% respectively. A decrease in the density and viscosity of the HDO liquid on increasing temperature was also observed, suggesting further cracking of heavier compounds as well [44].

Increase in temperature also led to a reduction in the acidity of the HDO liquid, due to the conversion of the carboxylic acids in the upgrading feedstock [45]. This suggests that the dominant pathway for the reduction of total acid number (TAN) is decarboxylation. The higher heating value of all HDO oils was within the range of 42.7±1.4 MJ/kg to 45.1±0.6 MJ/kg, with values being similar to those from other upgraded oil products [17,20,32].

The influence of hydrotreating temperature on the product composition can also be clearly seen in the gaseous phase. Longer residence times generally favored the production of C_{2+} gases, indicating further cracking activities [46]. The CO_2, CH_4 and N_2 composition of the products also increased at increasing temperature, with methane gas being the highest component in all gas streams.

Table 4.3 Properties of HDO liquids and gases.

Property	250°C 3h	300°C 1h	350°C 0.5h	350°C 1h
H2 consumption (mol/kg bio-oil)	44.9	44.9	44.6±0.6	45.4±1.1
Elemental Analysis (wt. %)				
C	84.2^{a}±0.0	85.4^{a}±0.3	83.2^{a}±1.9	86.5^{a}±0.1
H	13.1^{a}±0.0	$13.0^{a,}$±0.1	12.0^{b}±0.4	$12.7^{b,a}$±0.2
N	0.6^{a}±0.0	0.9^{a}±0.1	0.9^{a}±0.3	0.6^{a}±0.1
S	0.1^{a}±0.0	0.1^{a} ±0.0	0.1^{a} ±0.0	0.1^{a} ±0.0
O*	2.2^{a} ±0.0	0.6^{a}±0.1	3.9^{a} ±2.7	0.4^{a}±0.2

HHV (MJ/kg)	44.5^{b,a}±0.0	45.1^{a}±0.0	42.7^{b}±1.4	45.1^{a}±0.6
TAN (mg KOH/g)	4.0^{b}±0.1	7.4^{a}±0.4	3.3^{b}±0.1	1.9^{c}±0.1
Density (g/cc)	0.9^{a}±0.0	0.9^{a}±0.0	0.8^{a}±0.0	0.8^{a}±0.0
Viscosity (mm^2/s)	17.0^{a}±1.7	13.0^{a}±1.9	6.3^{b}±0.2	5.6^{b}±0.2
Gas composition (mole %) – Hydrogen free basis				
CO_2	4.7	6.2	8.7±0.8	11.0±0.2
CH_4	52.0	57.8	65.7±0.3	55.4±0.1
N_2	5.4	5.4	8.4±0.9	6.8±0.2
C_{2+}	38.0	30.6	17.2±2.0	26.8±0.4

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

The ultimate properties (Table 4.4) of the solid fractions from the respective hydrotreating studies showed that the co-upgrading process did not effectively strip the solid phase of the C species (carbon content ranged from 55.7 wt.% to 65.6 wt.%). The elemental and higher heating value properties of the solid fractions are very comparable, and there was no significant difference between them.

Table 4.4 Ultimate and higher heating value analysis of the HDO solid phase

Property	250°C 3h solid	300°C 1h solid	350°C 0.5h solid	350°C 1h solid
Elemental wt. %)				
C	55.7^{a}±1.9	59.7^{a} ±1.5	65.6^{a}±3.1	59.8^{a} ±3.0
H	7.9^{a}±0.1	8.5^{a}±0.8	9.2^{a}±0.9	8.7^{a}±0.6
N	3.4^{a} ±0.1	3.2^{a}±0.7	2.4^{a}±0.5	2.5^{a}±0.5
S	0.4^{a}±0.1	0.3^{a}±0.0	0.3^{a}±0.1	0.4^{a}±0.0
O*	32.7^{a}±2.0	28.4^{a}±1.6	22.6^{a}±3.5	28.6^{a}±3.1
HHV (MJ/kg)	24.5^{a}±0.9	27.4^{a}±1.9	31.4^{a}±3.0	27.7^{a}±2.5

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

The pyrolytic behavior of the HDO liquids and solids was studied, and the results can be seen in Figures 4.3 and 4.4. The mass loss rates are affected by hydrotreating temperature and time. The HDO liquid obtained from hydrotreating at 350°C and 30mins recorded the greatest mass loss rate at 276.9°C, with a further mass loss observed at 523.52°C before being suppressed. This suggests that the HDO liquid at this operating condition contained the highest amount of volatile matter, while the liquid obtained at 300°C and 1h contained the least amount of volatile matter [47]. The HDO liquid obtained at 350°C and 1h maintained the same pyrolytic behavior as the liquid at 30min, but decomposition ended earlier and with a significant amount of residue (21.5%). The thermal behavior of the obtained liquids was compared with commercial diesel for suitability for liquid fuel purposes. The weight loss of commercial diesel occurred only at one stage (kicked off at 232.8ºC and ended at 299.6°C)), after which 95.4 wt. % of the product had been valorized. Fuel combustion is an important property of liquid transportation fuels, as it helps to prevent uneven explosion and knocking [48]. To be able to use the obtained liquids as-is, ignition influencers such as alcohols and Di-Tetra-Butyl-Phenol (DTBP) are necessary [49-50]. The HDO liquid obtained from treatment at 350ºC and 0.5h contained the highest amount of volatile matter as a result of having the highest mass loss after commercial diesel. Therefore, further scenarios under 350°C and 0.5h was further studied.

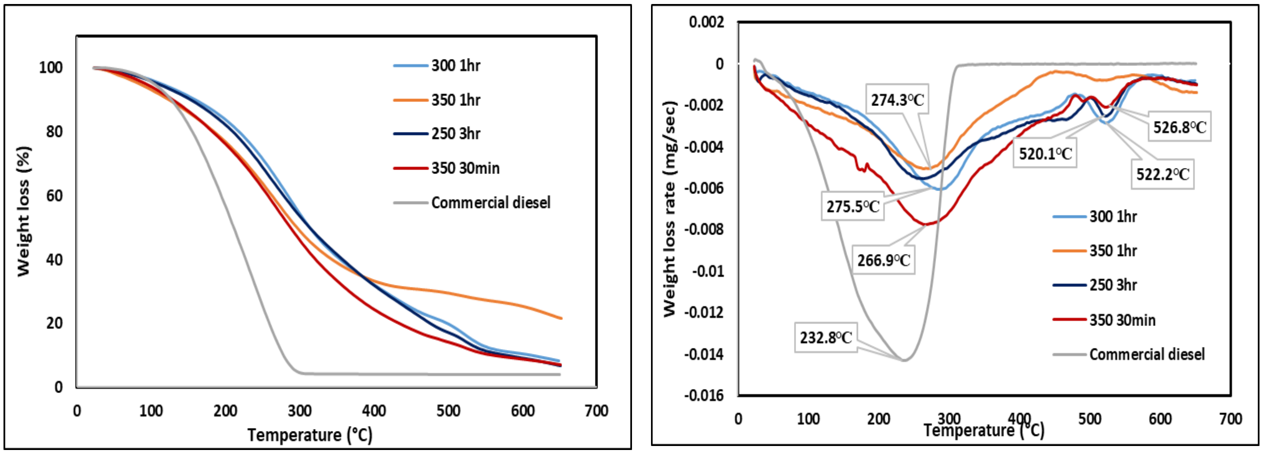

Figure 4.3 TGA and DTG of HDO liquids

From the DTG curve in Figure 4.4, it can be seen that the solid products had at least two degradation peaks each. The earliest weight loss in all samples was observed in the 300 1h solid at 176.3ºC, thus confirming the absence of water in all products. This solid can be said the said to be the most stable as well, due to having the highest peak loss at 499.6°C with a residue of 49.3 wt. %.

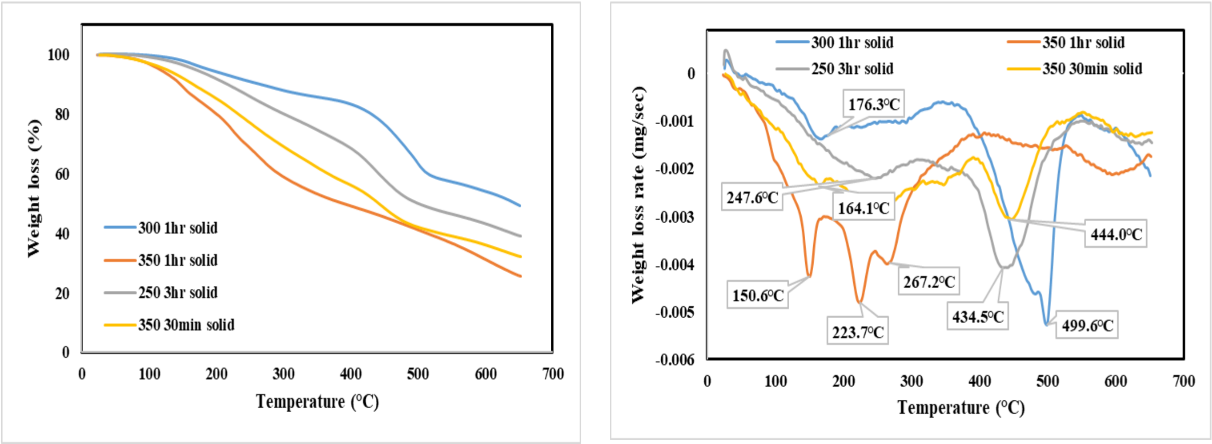

Figure 4.4 TG and DTG of HDO solids

4.4.3 Effect of process parameters on the yield and quality of HDO products

In optimizing the product quality at the 350ºC and 0.5h, there is a need to consider the influence of operating parameters and catalyst loading on the derived fractions.

4.4.3.1 Influence of Ni/SiO_2-Al_2O_3 catalyst

The effect of the Ni/silica alumina catalyst on the yield of HDO products obtained at 350°C and 0.5h can be seen in Figure 4.5 below.

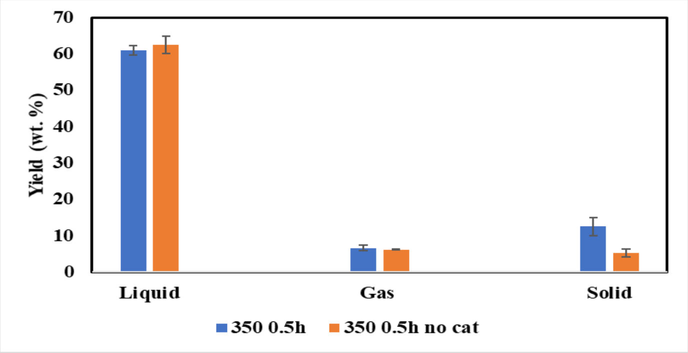

Figure 4.5 Yield comparison between catalytic and non-catalytic HDO products

There was no significant difference in the liquid and gaseous yields of the various product fractions from the catalytic and non-catalytic runs. The solid yield of the non-catalytic run (5.25±1.06 wt.%) varied significantly from that of the catalytic HDO (12.5±2.5 wt.%) however. The mass loss from both conditions: 19.8 % for 350°C 0.5h and 26.1% for 350ºC 0.5h when no catalyst was used; also varied significantly. The ultimate and the fuel properties of the liquids were also compared, and this can be seen in Table 4.5. The hydrogen gas consumption for the non-catalytic HDO was similar to the catalytic hydrotreatment, which might be as a result of similar processing times [14]. The elemental and higher heating value properties of the liquid products were comparable as well. The Total acid number (TAN) observed in the catalytic HDO (3.3±0.1) was slightly better than in the non-catalytic HDO (5.9±0.3), suggesting that the catalyst helped in saturating the carboxylic acid groups present [51]. Furthermore, the methane gas produced during the catalytic HDO was significantly higher than observed in the non-catalytic HDO. This could mean that the Ni catalyst favored higher demethylation of the methoxy groups present in the feed, which would have suppressed the possible carbon yield in the oil phase [52].

Table 4.5 Ultimate and fuel properties of catalytic and non-catalytic HDO liquids

Property	350°C 0.5h	350°C 0.5h no catalyst
H_2 consumption (mol/kg bio-oil)	$44.6^a \pm 0.6$	$43.6^a \pm 1.3$
Elemental Analysis (wt. %)		
C	$83.2^a \pm 1.9$	$85.9^a \pm 0.6$
H	$12.0^a \pm 0.4$	$12.6^a \pm 0.1$
N	$0.9^a \pm 0.3$	$0.9^a \pm 0.2$
S	$0.1^a \pm 0.0$	$0.1^a \pm 0.0$
O*	$3.9^a \pm 2.7$	$0.6^a \pm 0.5$
HHV (MJ/kg)	$42.7^a \pm 1.4$	$44.7^a \pm 0.3$
TAN (mg KOH/g)	$3.3^a \pm 0.1$	$5.9^a \pm 0.3$
Density (g/cc)	$0.8^a \pm 0.0$	$0.8^a \pm 0.0$
Viscosity (mm^2/s)	$6.3^a \pm 0.2$	$7.4^a \pm 0.4$
Gas composition (mole %) – Hydrogen free basis		
CO_2	$8.7^a \pm 0.8$	$12.6^a \pm 2.8$
CH_4	$65.7^a \pm 0.3$	$59.9^b \pm 1.7$
N_2	$8.4^a \pm 0.9$	$7.8^a \pm 0.2$
C_{2+}	$17.2^a \pm 2.0$	$19.7^a \pm 4.3$

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

The result from the thermal behavior study of both liquid products is presented in Figure 4.6. The first weight loss for the non-catalytic liquid product occurred at 291.6ºC, as compared to 263.6°C for the catalytic HDO liquid. At this temperature, 47.5 wt. % had pyrolyzed in the non-catalytic HDO liquid as compared to 42.1 wt.% in the catalytic liquid. At the second weight loss temperatures of 526.8ºC and 528.3°C for the catalytic and non-catalytic liquids respectively, 86.3 wt. % and 88 wt. % had pyrolyzed. Both oils can thus be said to exhibit the same heating behavior.

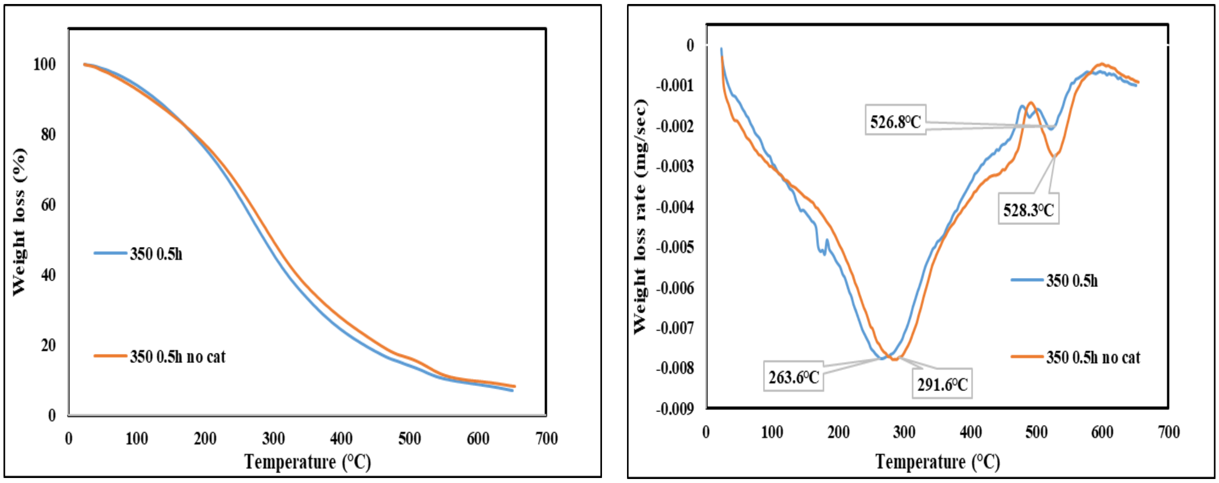

Figure 4.6 TGA and DTG of HDO liquids from catalyzed and non-catalyzed hydrotreating

The properties of the solid products from both fractions is presented in Table 4.6. The ultimate and higher heating value properties can be seen to be very comparable. This suggests that the cracked oil could be behaving as a sort of catalyst in the absence of Ni/silica-alumina. The thermal behavior of the solids was also compared, and can be seen in Figure A4.3. The solid fractions were comparable as well, although there was more residue in the non-catalytic HDO solid (38.2%) in comparison with the solids obtained over silica alumina catalyst (32.3%).

Table 4.6 Ultimate and higher heating value analysis of catalyzed and non-catalyzed HDO solid products

Property	350°C 0.5h solid	350°C 0.5h no cat solid
Elemental (wt. %)		
C	65.6^{a}±3.1	56.1^{a}±3.8
H	9.2^{a}±0.9	6.0^{a}±1.5
N	2.4^{a}±0.5	3.7^{a}±0.0
S	0.3^{a}±0.1	0.3^{a}±0.2
O*	22.6^{a}±3.5	34.1^{a}±5.1
HHV (MJ/kg)	31.4^{a}±3.0	21.5^{a}±4.3

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

4.4.3.2 Influence of catalyst loading

The effect of increased catalyst loading rate from 2.5% to 5% on the HDO product yield can be seen in Figure 4.7 below. The yield of the HDO liquids (61.0±1.3 wt.% for 350 0.5h and 59.8±2.47 wt.% for 350 0.5h 5% cat) were very comparable, although significantly different yields of solid and gaseous fractions were obtained. The mass loss obtained from increasing the catalyst loading was 5.5%, which was significantly different to the 2.5% catalyst loading (19.8%).

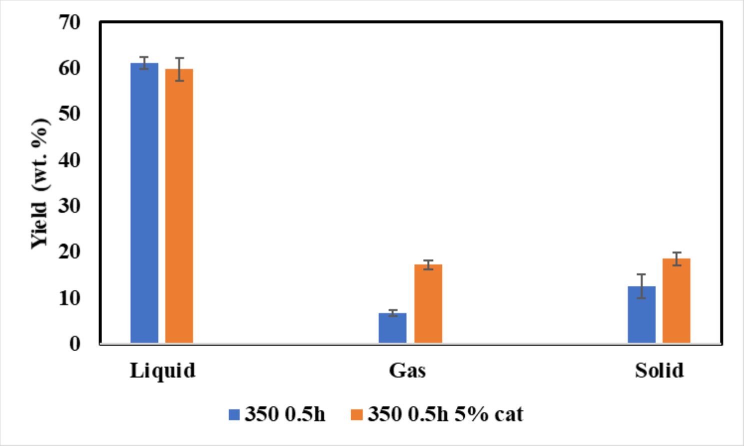

Figure 4.7 Product yield from increased loading of catalyst

The ultimate and fuel properties of the HDO liquids is presented in Table 4.7. The liquid improved in acidity on increased catalyst loading, suggesting more successful removal of heavier compounds from this phase [53]. There was higher sulfur content (0.2±0.0 wt. %) in the resulting liquid however, suggesting that increased catalyst loading might be more effective for hydrodeoxygenation than hydrodesulfurization. The produced gas also had a comparably higher fraction of C_{2+} (higher alkanes such as ethane and propane), possibly due to higher cracking activities [36]. There was, however, a reduction in the methane and nitrogen species composition suggesting that methanation is not a dominant pathway on increased catalyst loading.

The thermal behavior of these liquids is presented in Figure 4.8. The first mass loss from the increased catalyst loading was observed at 281.6°C, compared to 263.6°C from the 2.5 wt. % catalyst loading. During this time, 51.5% of the liquid had burnt compared with 42.1 wt. % observed in the 2.5wt. % catalyst loading run. This signifies an improved fuel burning property, although it is still widely disproportionate from what was observed in the commercial diesel (95.4 wt.%

Table 4.7 Ultimate and fuel properties of HDO liquids from increased catalyst loading

Property	350°C 0.5h	350°C 0.5h 5% cat
H2 consumption (mol/kg bio-oil)	44.6^{a}±0.6	46.7^{a}±0.1
Elemental Analysis (wt. %)		
C	83.2^{a}±1.9	83.2^{a}±1.4
H	12.0^{a}±0.4	13.0^{a} ±1.2
N	0.9^{a}±0.3	0.8^{a}±0.1
S	0.1^{b}±0.0	0.2^{a}±0.0
O*	3.9^{a}±2.7	2.9^{a}±0.1
HHV (MJ/kg)	42.7^{a}±1.4	44.1^{a}±2.2
TAN (mg KOH/g)	3.3^{a}±0.1	2.3^{b}±0.0
Density (g/cc)	0.8^{a}±0.0	0.8^{a}±0.1
Viscosity (mm^{2}/s)	6.3^{a}±0.2	5.8^{a}±0.1
Gas composition (mole %) – Hydrogen free basis		
CO_2	8.7^{a}±0.8	8.4^{a}±1.3
CH_4	65.7^{a}±0.3	52.4^{b}±1.2
N_2	8.4^{a}±0.9	2.9^{b}±0.6
C_{2+}	17.2^{b}±2.0	36.3^{a}±0.8

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

At the second stage of decomposition, 90.84 wt.% of the HDO liquid from the increased catalyst loading had valorized compared with 86.3 wt. % at 526.8ºC observed in the liquid from the lower catalyst loading. The amount of final residue was also slightly lower: 4.7 wt.% for the increased catalyst loading as against 7.1 wt.% in the lower loading. It can therefore be said that increased catalyst loading resulted in the production of a liquid with slightly better thermal properties

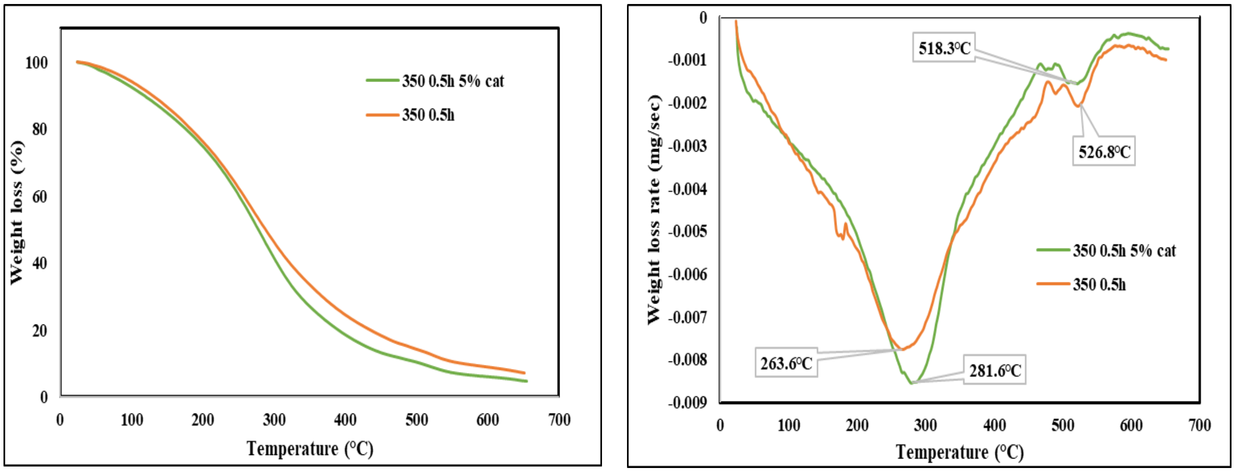

Figure 4.8 TGA and DTG of HDO liquid from increased catalyst loading

The ultimate analysis of the solid phase was comparable to the solid obtained using a catalyst loading of 2.5wt%, although an increased oxygen content was observed. This suggests the higher activation of the solid is achieved at higher catalyst loading, due to the creation of surface oxygen functional groups [54]. The thermal stability of the obtained liquid and product phases were comparable with previous products as well (as seen in Figure A4.4), with a slightly higher solid residue (36.6%) than observed in the solid obtained from 2.5% loading of catalyst (32.3%).

Table 4.8 Ultimate and higher heating value analysis of HDO solid from increased catalyst loading

Property	350°C 0.5h solid	350°C 0.5h 5% cat solid
Elemental (wt. %)		
C	65.6^{a}±3.1	56.5^{a}±0.8
H	9.2^{a}±0.9	8.3^{a}±0.1
N	2.4^{a}±0.5	2.4^{a}±0.0
S	0.3^{a}±0.1	0.3^{a}±0.1
O*	22.6^{a}±3.5	32.5^{a}±0.8
HHV (MJ/kg)	31.4^{a}±3.0	25.2^{b}±0.5

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard ±deviation.

4.4.3.3 Influence of uncracked oil on HDO product quality

The effect of using highly viscous and uncracked carinata oil as opposed to oil in which the carboxylic acid groups have undergone cleavage activities is presented in Figure 4.9. The properties of the uncracked oil (as seen in Table A4.1) suggests the presence of high amounts of carboxylic acids typical of triglycerides, which results in an elemental oxygen content of 17.9±2.2 wt.%. This result was also compared to an hydrotreating run using a model erucic acid, as this was the highest fatty acid present in the carinata oil profile.

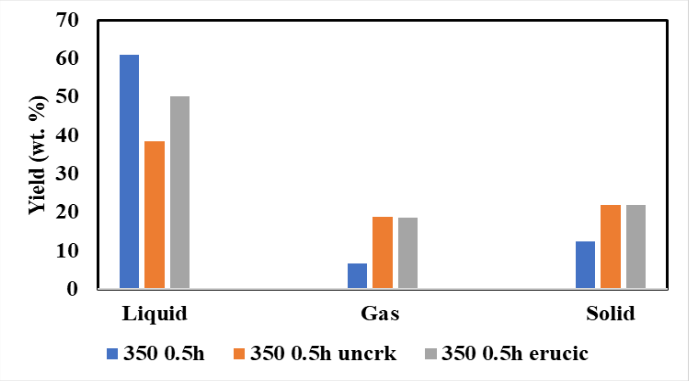

Figure 4.9 Product yields from using uncracked oil

The obtained oil yields were significantly lower than previous experiments, although higher gas and solid production were obtained. This was as a result of higher carbon alkanes in the gaseous phase, which is likely due to the formation of more propane from the hydrogenation of glycerin fraction [55]. The mass loss observed in the HDO run using erucic acid (9.3 wt. %) was significantly different compared with 350°C 0.5h (19.8 wt. %) and the use of uncracked carinata oil (20.6 wt. %). The ultimate and fuel properties of the various liquid and gaseous products is presented in Table 4.9. The presence of low oxygen in the produced oil also suggests that a decarbonylation reaction might be active, which could be the reason for lower hydrogen consumption.

Table 4.9 Properties of the oil and gas fractions from the uncracked and thermal cracking experiments

Property	350°C 0.5h cracked HDO solid	350°C 0.5h uncracked HDO solid	350°C 0.5h erucic HDO solid
H_2 consumption (mol/kg bio-oil)	$44.55^{a}\pm0.55$	34.4	35.1
Elemental Analysis (wt. %)			
C	$83.21^{a}\pm1.9$	$82.7^{a}\pm0.1$	$82.7^{a}\pm1.6$
H	$12.0^{a}\pm0.4$	$13.8^{a}\pm0.3$	$13.4^{a}\pm0.4$
N	$0.86^{a}\pm0.3$	$1.0^{a}\pm0.4$	$0.7^{a}\pm0.0$
S	$0.08^{b}\pm0.0$	$0.3^{a}\pm0.1$	$0.2^{a}\pm0.1$
O	$3.90^{a}\pm2.7$	$2.2^{a}\pm0.1$	$3.0^{a}\pm1.1$
HHV (MJ/kg)	$42.71^{a}\pm1.4$	$45.0^{a}\pm0.3$	$44.4^{a}\pm0.2$
TAN (mg KOH/g)	$3.31^{a}\pm0.1$	$0.9^{c}\pm0.1$	$2.1^{b}\pm0.3$
Density (g/cc)	$0.8^{a}\pm0.0$	$0.8^{a}\pm0.0$	$0.8^{a}\pm0.0$
Viscosity (mm^2/s)	$6.3^{a}\pm0.2$	$4.0^{b}\pm0.3$	$4.3^{b}\pm0.2$
Gas composition (mole %)			
CO_2	8.7±0.8	8.8	3.1

CH_4	65.7±0.3	57.8	26.2
N_2	8.4±0.9	2.3	0.6
C_{2+}	17.2±2.0	31.2	69.9

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

The presence of lower methane and higher carbon species in the gas phases from both the use of uncracked oil and erucic acid suggests lower methanation and higher cracking at these conditions. The thermal stability of the derived liquids were also compared, and this can be seen in Figure 4.10.

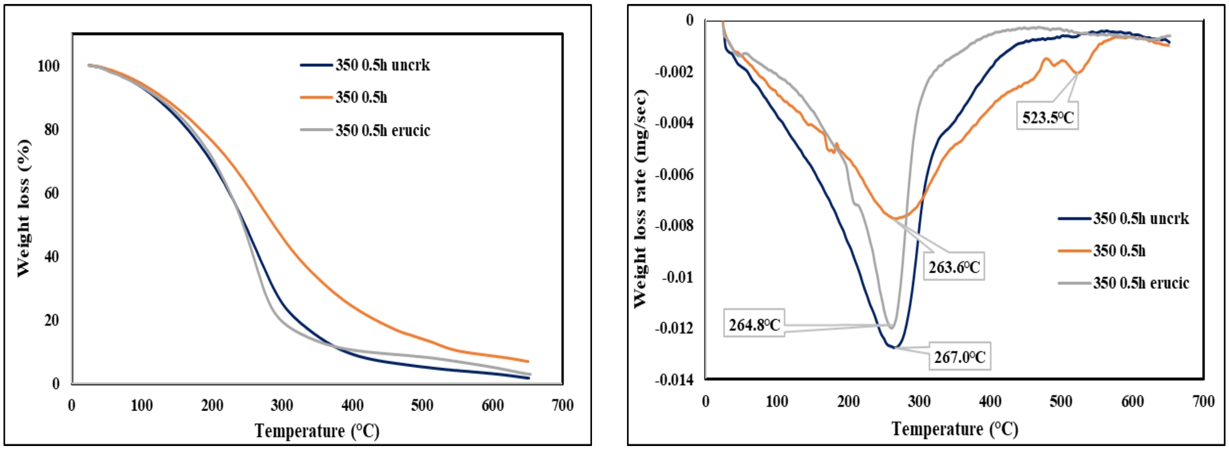

Figure 4.10 TGA and DTG of HDO liquids from the use of uncraked non-edible oils

The thermogram suggests that the uncracked oil and erucic acid contain more of volatile compounds in the liquid phase. This is not necessarily an excellent result, considering the fact that there are significant amounts of sulfur is present in the liquids. This therefore represent an added cost to remove the environmental impacts of sulfur oxides. The ultimate properties and higher heating values of the solid products is presented in Table 4.10.

Table 4.10 Ultimate and higher heating value analysis of HDO solids using uncracked oils

Property	350°C 0.5h cracked HDO solid	350°C 0.5h uncracked HDO solid	350°C 0.5h erucic HDO solid
Elemental (wt. %)			
C	65.6^a±3.1	51.2^b±1.9	43.5^b±2.9
H	9.2^a±0.9	7.4^a±1.2	8.4^a±0.2
N	2.4^a±0.5	3.1^a±0.0	2.1^a±0.2
S	0.3^a±0.1	0.1^a±0.0	0.5^a±0.1
O*	22.6^b±3.5	38.3^a±0.7	45.5^a±2.4
HHV (MJ/kg)	31.4^a±3.0	21.1^b±1.0	18.7^b±1.1

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

The presence of large amounts of elemental oxygen could present a significant challenge, if stable oxides are formed. This could result in the blockage of active sites in the catalyst's pores, thereby resulting in deactivation. The thermal stability of the solids was also examined (Fig A4.5). The solid from the uncracked oil and erucic acid hyrotreatment reactions were comparable, and exhibited similar thermal degradation. They also produced slightly higher amounts of residue (37wt. % for uncracked oil and 36.2 wt.% for erucic acid) as compared to 32.3 wt.% for the solid from cracked oil.

4.4.3.4 Influence of initial nitrogen pressure

The effect of thermal treatments in nitrogen environments with/without catalyst was also studied to possibly understand the role of the Ni/silica-alumina catalyst. The result is presented in Figure 4.11.

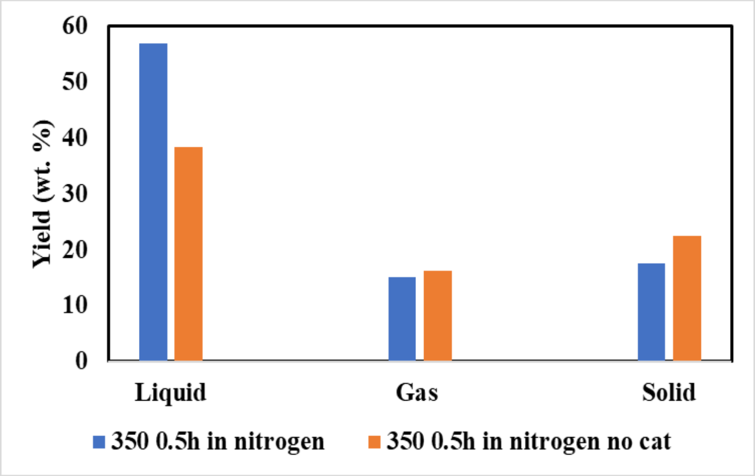

Figure 4.11 Product yield from cracking in nitrogen

The influence of the catalyst in increasing liquid yield while reducing the solid and gaseous yields can clearly be seen. There was a significant (47.8 %) increase in liquid yield, from 38.4 wt.% when the catalyst was not used, to 56.8 wt.% with Ni/silica-alumina catalyst. Mass was also significantly conserved when the catalyst was used, with a mass loss of 10.6 wt.% observed when the catalyst was used as compared to 22.8 wt.% without catalyst.

The ultimate and fuel properties of both HDO liquids is presented in Table 4.11. The significant (64.8 wt. %) reduction in the elemental oxygen content on catalyst use portrays the versatility of this catalyst in hydrodeoxygenation. The dominant methanation reactions in the gaseous phase was also observed, as the use of catalyst increased the methane gas production from 47.9 mole % to 54.2 mole %. The thermal properties of the obtained liquid were also studied, and can be seen in Figure 4.12.

Table 4.11 Ultimate and fuel properties of HDO liquids in nitrogen environment

Property	350°C 0.5h in nitrogen	350°C 0.5h in nitrogen no cat
Elemental Analysis (wt. %)		
C	84.7^{a}±0.8	82.5^{a}±1.5
H	12.2^{a}±0.2	11.5^{b}±0.0
N	1.0^{a}±0.2	0.6^{a}±0.1

S	$0.2^{a}\pm0.0$	$0.1^{b}\pm0.0$
O*	$1.9^{b}\pm0.8$	$5.4^{a}\pm1.6$
HHV (MJ/kg)	$43.8^{a}\pm0.6$	$41.8^{a}\pm0.7$
TAN (mg KOH/g)	$2.3^{a}\pm0.2$	$2.2^{a}\pm0.2$
Density (g/cc)	$0.8^{a}\pm0.0$	$0.8^{a}\pm0.0$
Viscosity (mm^2/s)	$4.2^{a}\pm0.2$	$2.5^{b}\pm0.1$
Gas composition (mole %) – Nitrogen free basis		
CO_2	3.1	2.3
CH_4	54.2	47.9
H_2	24.0	31.1
C_{2+}	18.8	18.7

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

The inability of further assisted cracking through the use of catalyst could explain the reason for the higher volatile matter in the HDO liquid obtained without the catalyst. This explains the presence of higher oxygen in this liquid product.

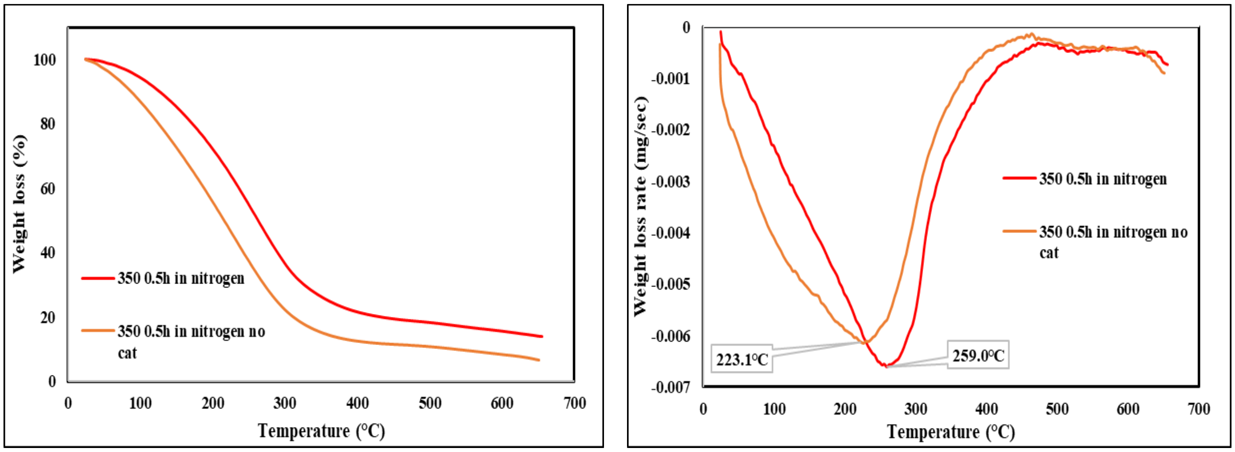

Figure 4.12 TGA and DTG of HDO liquids obtained from thermal treatments under nitrogen

The elemental properties and higher heating values of the solid products is reported in Table 4.12. The effectiveness of the catalyst in the generation of liquid and solid products can be seen in the reduced elemental oxygen present in the solid phase. The presence of considerable carbon in this phase also suggests that catalyst regeneration might be very much possible, with the possibility of increased product yields. The thermal properties of the solid products were also studied, and can be seen in Figure A4.6. The solid from the catalyzed thermal treatment under nitrogen had slightly higher thermal stability, and had two major mass loss points. At the first mass loss point of 230.9ºC, 21.8 wt. % of the solid had volatilized as compared to 21.5 wt. % at 194.1ºC. At the second mass loss point of 484.9°C, 41.4 wt. % of this solid had burned compared with 42.65 wt. % at 404.2°C.

Table 4.12 Ultimate and higher heating value analysis of HDO solids in nitrogen environment

Property	350°C 0.5h in nitrogen solid	350°C 0.5h in nitrogen no cat solid
Elemental (wt. %)		
C	$60.3^{a}\pm1.1$	$33.6^{b}\pm0.1$
H	$7.1^{a}\pm1.0$	$7.5^{a}\pm0.6$
N	$2.1^{b}\pm0.0$	$2.3^{a}\pm0.0$
S	$0.5^{a}\pm0.1$	$0.4^{a}\pm0.0$
O*	$30.1^{b}\pm2.2$	$56.2^{a}\pm0.8$
HHV (MJ/kg)	$25.2^{a}\pm2.1$	$12.1^{b}\pm1.1$

*: calculated by difference. Different alphabets in the superscript of each column denote that the values are significantly different for each operating condition. Values after ± denote standard deviation.

4.4.4 Functional group analysis of HDO liquids

The Fourier transform infrared spectroscopy (FTIR) was used to further understand the structural changes that occurred during the co-hydrotreating of sludge biocrude and cracked carinata oil, and functional group identification was carried out based on previous studies [36,56]. Prior ring opening effects of using a cracked and coupled with the reduction in the intensity of CH_2 and CH_3 vibrations at 1500 to 1300cm^{-1} resulted in an HDO liquids that was functionally like commercial diesel fuels. As can be seen in Figure 4.13, the structure of the liquids produced using the 350 30mins and 300 1hr were similar to commercial diesel fuel. The peaks observed between 3000 and 3650 can be ascribed to –OH stretching vibrations as a result of the presence of phenolic compounds and alcohols. These peaks can be seen to disappear in the commercial diesel, and the benchmark liquids (350 30mins and 3001hr) also exhibited this trend. Furthermore, the peaks noticed in these products around 2100cm^{-1} might be an indication of the presence of nitriles in these products, despite showing better nitrogen removal from ultimate analysis [57].

The influence of various operating scenarios on the optimum processing condition of 350 30mins did not significantly alter the structure of the HDO liquid produced, as can be seen in Figure A4.7 (provided in supplementary data). In the liquid product obtained using the uncracked carinata oil however, a large peak was observed at 1710cm^{-1}. This corresponds to the presence of carbonyl group stretching vibrations at this point, an indication of incomplete hydrodeoxygenation which could be due to the product of aldehydes and ketones.

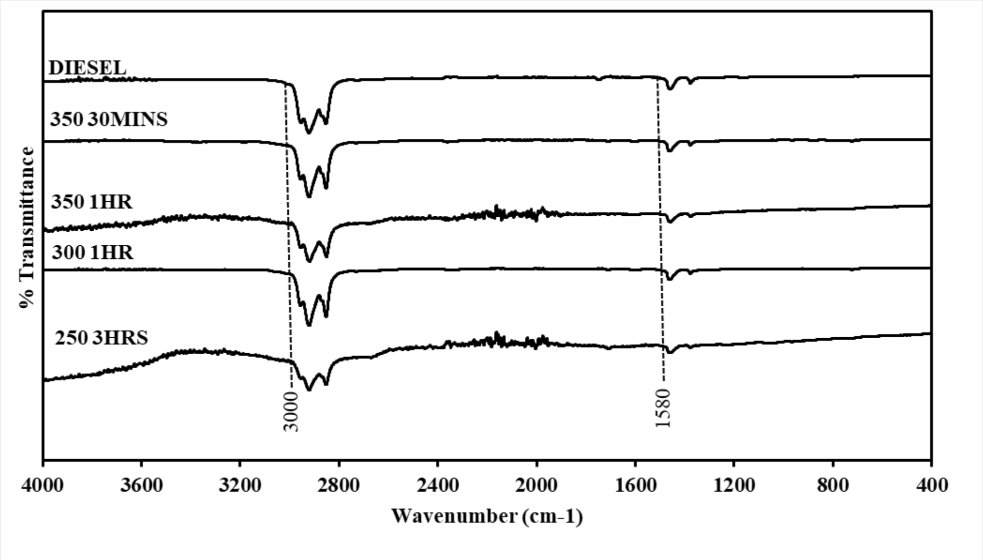

Figure 4.13 FTIR spectra comparison of produced liquids with commercial diesel

4.5 Conclusions

Hydrodeoxygenation study using commercial Ni/SiO_2-Al_2O_3 catalyst was performed with a mixture of municipal sludge and cracked *Brassica carinata* oil. The HDO yielded a liquid fraction, as well as gaseous and solid products. Analysis of HDO fractions revealed the influence of hydrotreating temperature and processing time on the overall quality of the final product. Higher temperature favored the production of more liquid products, while longer processing times resulted in the production of more solid fractions. The alumina catalyst helped to generally improve the acidity (from 5.9±0.3 mg KOH/g when no catalyst was used, to 3.3±0.1 mg KOH/g), viscosity of the liquid fraction (from 7.4±0.4 cSt when no catalyst was used, to 6.3±0.2 cSt) and favored the production of lighter gas fractions (C_{2+} gas volumes of 19.7±4.3 mol % when no catalyst was used, to 17.2±2.0 mol %).

Increasing the catalyst loading from 2.5 wt.% to 5 wt.% slightly improved the acidity of the obtained liquid (from 3.3±0.1 mg KOH/g to 2.3±0.0 mg KOH/g) , but the solids yield significantly increased suggesting the quick deactivation of the alumina catalyst. The catalytic behavior of the cracked oil was observed during experiments ran without hydrogen and catalyst, respectively. There were significant improvements in the N and S removal percentages in these runs, and the obtained liquid had significantly lower viscosity and acidity. The hydrogen consumption observed in the hydrodeoxygenation experiment using model erucic acid was significantly lower than was observed in other experiments. The product yields were also not comparable, signifying that the model compound might not be an adequate representation of the *Brassica carinata* oil. This is a generally encouraging study into the possible co-upgrading of waste feedstocks, which could result in complementary improvement of these feedstocks. Future work should investigate cracking and upgrading using other heterogenous catalysts, in order to address the catalyst deactivation rate.

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Chapter 5

CONCLUSIONS

5.1 Conclusions

The production of biological fuels from municipal sludge has been demonstrated in this study. Municipal sludge is a viable feedstock that merits consideration for integration into the Bioeconomy. Sludge is a byproduct of wastewater treatment processes at treatment works and is an agglomeration of various organic matter. Current treatment processes have not been effective in valorizing this waste stream without added adverse effects.

Catalysts represent a significant cost in conversion processes, with a potential cost of $1.3 million on an annual basis. Research into low cost catalytic options for industrial conversion processes is therefore a significant and cost-cutting approach. Red clay is formed as a result of chemical weathering processes that take place over long periods of time.

This research study was conducted to 1) evaluate the effect of red clay catalyst on the liquefaction of municipal sludge. The hydrothermal liquefaction of different sludge types has been documented to contain considerable amounts of heteroatoms (N, O and S). This present a significant challenge in the bid to produce liquid transportation fuels from sludge biocrudes. The presence of these heteroatoms ensures that the produced biocrudes have high acidity and release toxic NOx compounds on combustion. Upgrading of these crudes is therefore a necessity.

Waste cooking and non-edible oils are triglycerides with potential to produce commercial ready drop-in fuels. Previous studies have reported fuel products synthesized from feedstocks of this nature can be readily processed with petroleum-based products, thus providing a cost-effective approach to upgrade fuels. Catalytic cracking is a low-temperature ring opening process that helps to ensure that triglycerides become fuel ready by rapidly improving the viscosity and the higher heating value. Co-upgrading sludge biocrudes and cracked oils could help to upgrade two waste fuel products while regulating the hydrogen consumption. Silica on alumina catalysts doped with metals have been found to increase the yield of liquid products and produce fuels in the light diesel range. The second objective of this research was therefore to 2) study the effect of Ni/SiO_2-Al_2O_3 catalyst on the co-upgrading of sludge biocrude and cracked Carinata oil.

Objective 1: HTL of 3 sludge types (PD:Pre-dried, Sec: Secondary and Tk:Thickened) was carried out at 300°C and 325°C at 1hour residence time, initial nitrogen pressure loading of 0.65MPa and a stirring speed of 95RPM. The proximate and ultimate properties of these feedstocks were fairly comparable, although the ash contents, volatile matter contents, elemental carbon contents and higher heating values varied significantly.

Highest bio-oil yield of 37.7±1.6 wt.% was obtained in the thickened sludge at 325°C while the lowest yield of 21.5±1.3 wt.% was obtained in the secondary sludge at 300°C.The higher heating value obtained also ranged from 24.2±0.3 MJ/kg to 35.0±0.8 MJ/kg. The total acid number (TAN) was lowest (13.1±0.2 mg KOH/g) in the thickened sludge liquefied at 300°C while the highest (19.8±1.6 mg KOH/g) was observed in the secondary biocrude product at 325°C.

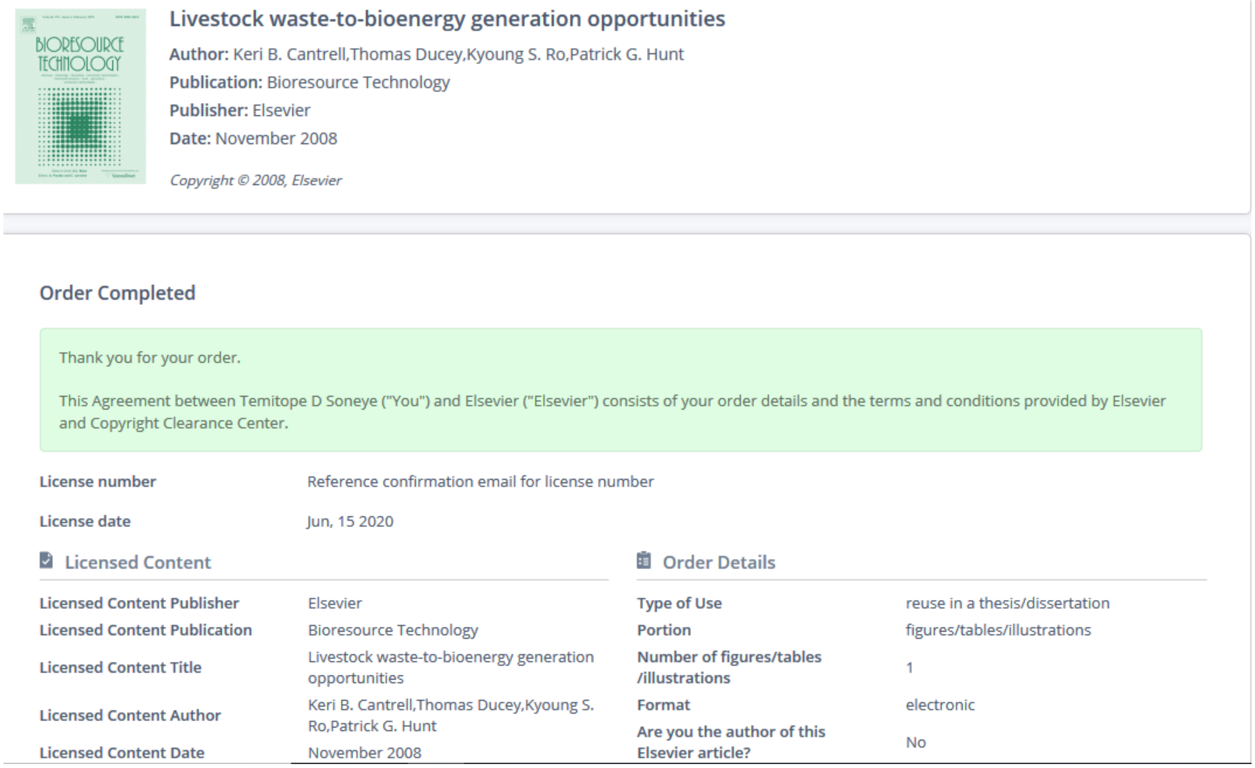
The chemical composition of the biocrudes obtained from the catalyzed and uncatalyzed runs were very much similar, with acids being the major constituents. The boiling point distribution of the biocrudes revealed that about 36 – 46% of the crude was in the heavy diesel (321°C - 425°C) range, with the catalyzed runs effecting the production of heavier fractions. The aqueous phase obtained from the liquefaction products was heavily polluted with nutrients, with high concentration of ammonia nitrogen and potassium ions, although the sulfate levels were high as well. The char products were of low higher heating value (5.1±0.1 MJ/kg to 10.0±0.1 MJ/kg) and could find use in the production of sludge based activated carbon for improved biocrude production. The gas yield also increased with increasing temperature, and heavier carbon species were the major products in all experiments.

These findings present encouraging results from the use of waste municipal sludge for energy production purposes. Future work should focus on sludge pretreatment efforts prior to liquefaction, to produce fuels that can be readily blended and processed with other crudes.

Objective 2: Co-upgrading of the HTL oil obtained from the pre-dried sludge at 325°C with cracked *B.carinata* oil over Ni/SiO_2-$Al_2O_3$for heteroatom removal at varied operating parameters was studied. The liquid yields obtained at 250°C hr, 300°C 1hr, 350°C 1hr, 350°C 30min did not vary significantly from each other. The experimental operating condition of 350°C 30min was found to be most efficient in terms of the overall product quality, and this was studied further. The role of the silica on alumina catalyst was discovered to be evident in the acidity improvement due to cracking of heavier compounds, as well as the production of more methane in the gaseous product. The increase in the catalyst loading rate resulted in the production of liquid fractions with improved viscosity and acidity, and the production of higher carbon gases due to further cracking of heavier compounds. Hydrotreating the feedstock in the absence of hydrogen resulted in slightly lower liquid yields, although an hydrogen donor-receptor relationship was observed between the municipal sludge biocrude and the cracked carinata oil. The use of uncracked oil as opposed to cracking resulted in significantly lower liquid yield with lesser hydrogen consumption, suggesting slower levels of hydrodeoxygenation. The liquid, however, had a significantly lower total acid number of 0.9±0.1 mg KOH/g. The use of the model erucic acid resulted in further lower liquid yield and markedly high amounts of higher carbon species in the gas phase.

The structural composition of the hydrotreating products from 3001hr and 350 30min were most comparable with commercial diesel fuel. The cracking of the carinata oil resulted in the disappearance of the C-O and C-O-C stretching vibrations normally observed within 1200 to 800 cm-1, while the CH2 and CH3 vibrations at 1500 to 1300cm-1 also reduced in intensity. This inferential ring opening properties provided by the cracking of the carinata oil were then transferred to the CRK HEBCO + HTL OIL mixture. There is need to carry out hydrotreating experiments using other heterogenous and sulfided catalysts, and catalyst recirculation should be studied.

APPENDIX



Livestock waste-to-bioenergy generation opportunities

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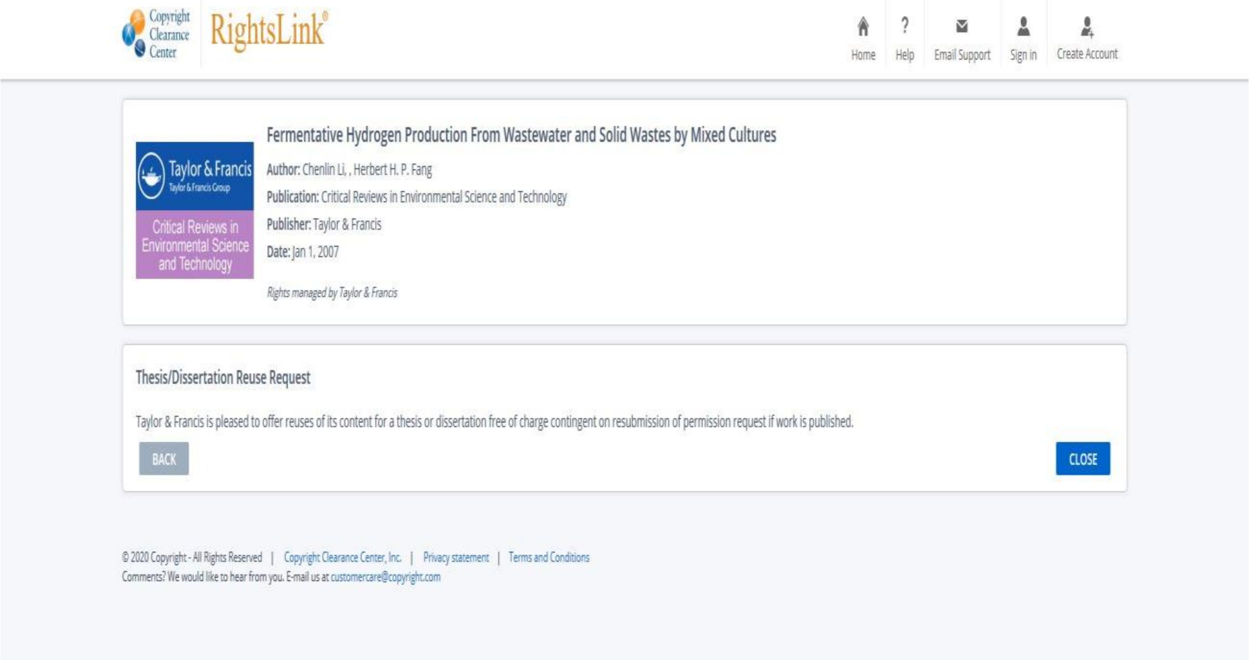

Fermentative Hydrogen Production From Wastewater and Solid Wastes by Mixed Cultures

Author: Chenlin Li, , Herbert H. P. Fang

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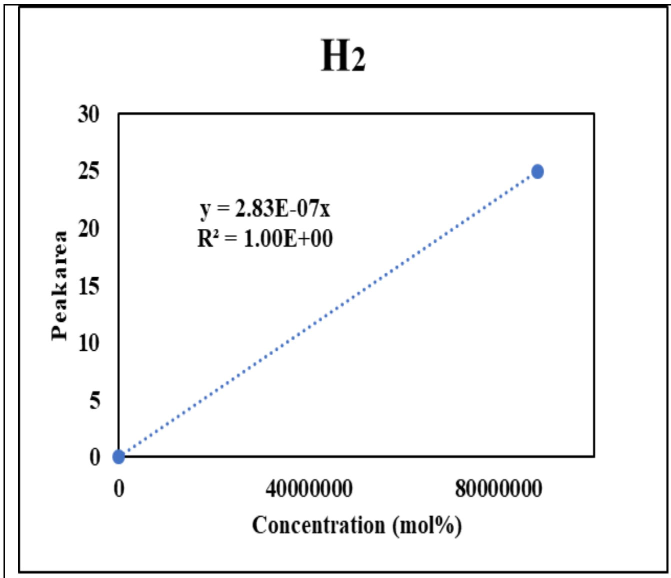
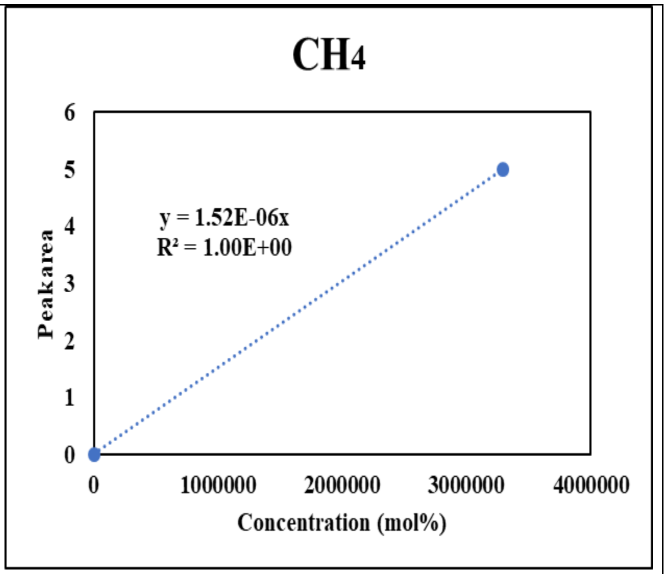
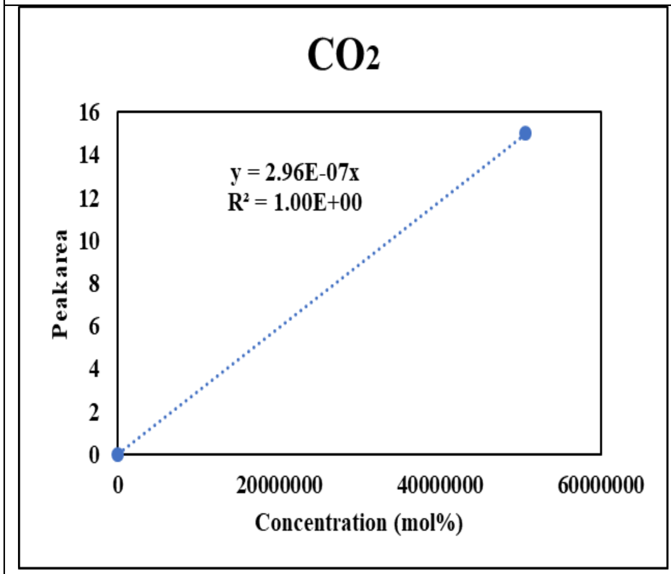
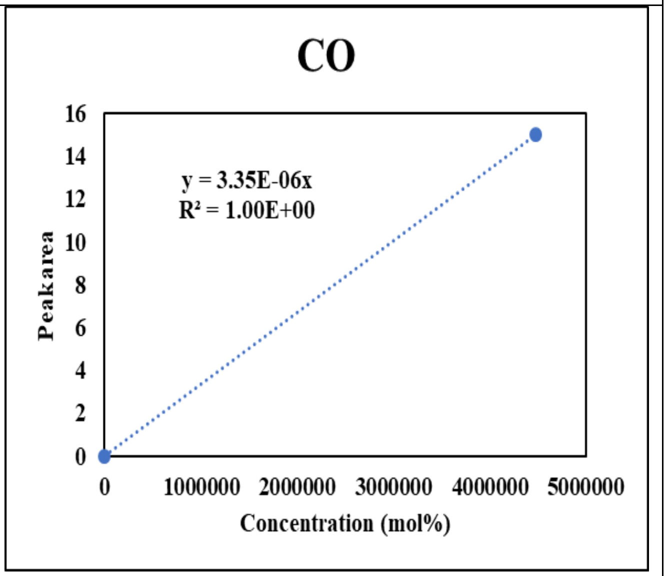
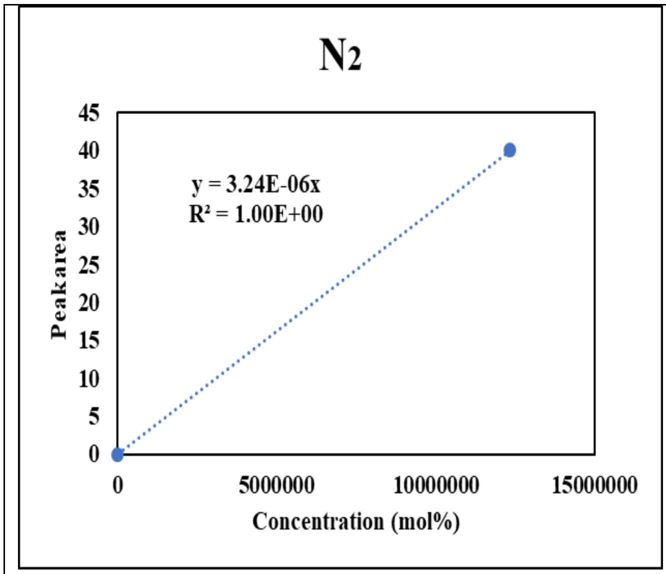
Table A.3 Micro-GC calibration curves











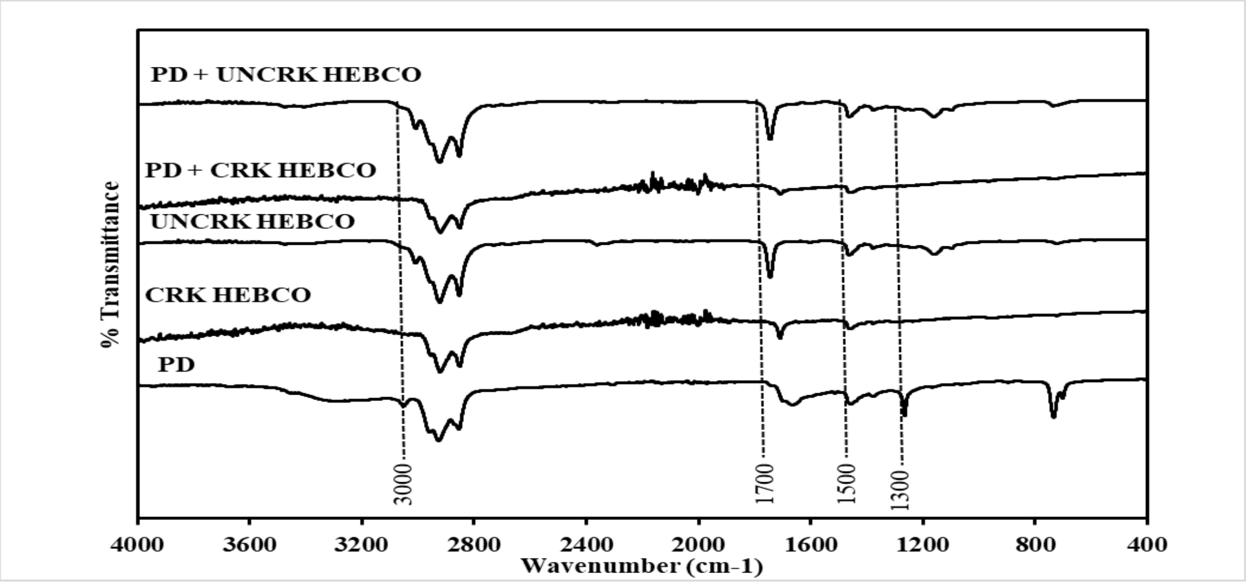


Figure A4.1 FT-IR spectra of the feedstocks used in this upgrading study

Figure A4.2 Liquid products from the hydrotreating of HTL oil in THF (left) and Butanol (right)

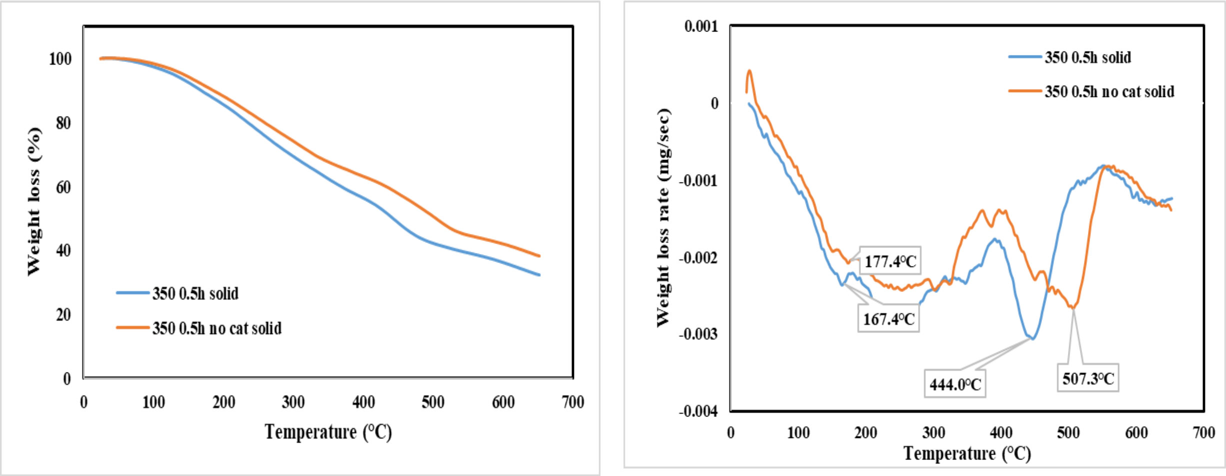


Figure A4.3 TGA and DTG of HDO solids from catalyzed and non-catalyzed hydrotreating

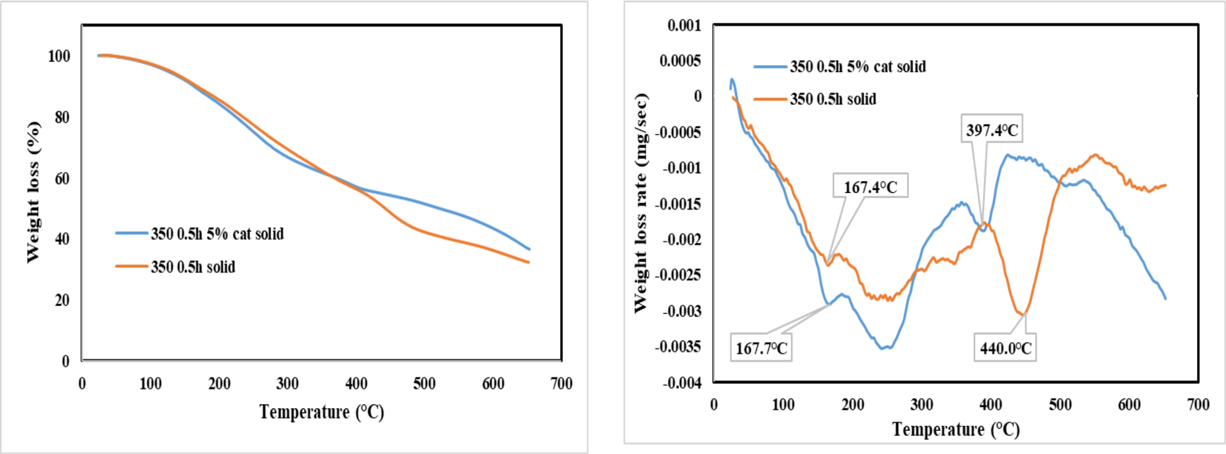


Figure A4.4 TGA and DTG of HDO solid from increased catalyst loading

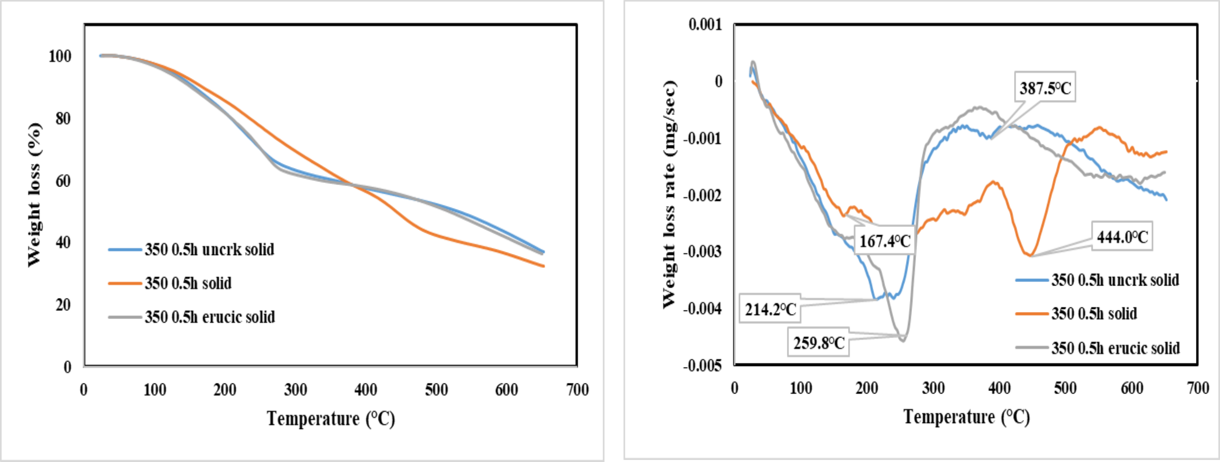


Figure A4.5 TGA and DTG of HDO solids from the use of uncracked non-edible oils

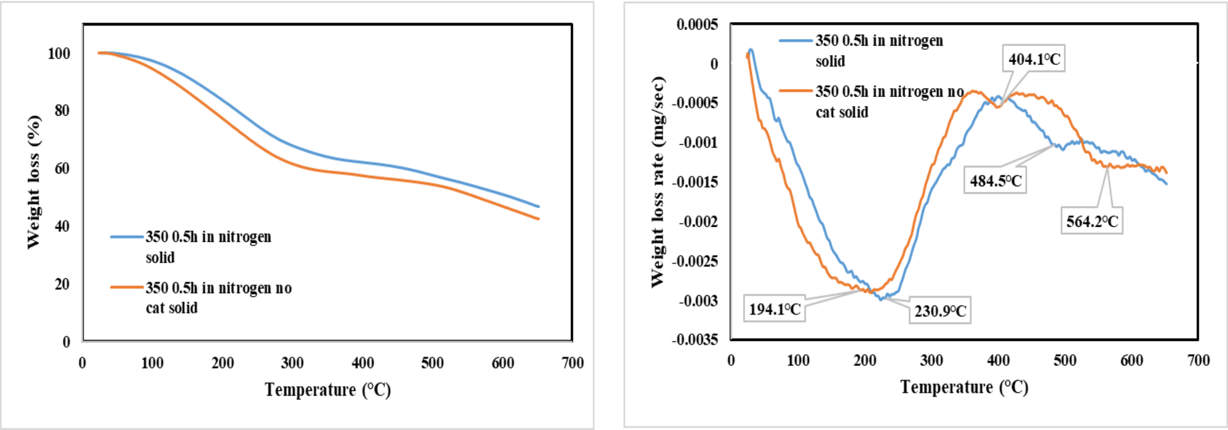


Figure A4.6 TGA and DTG of HDO solids obtained from thermal treatments under nitrogen

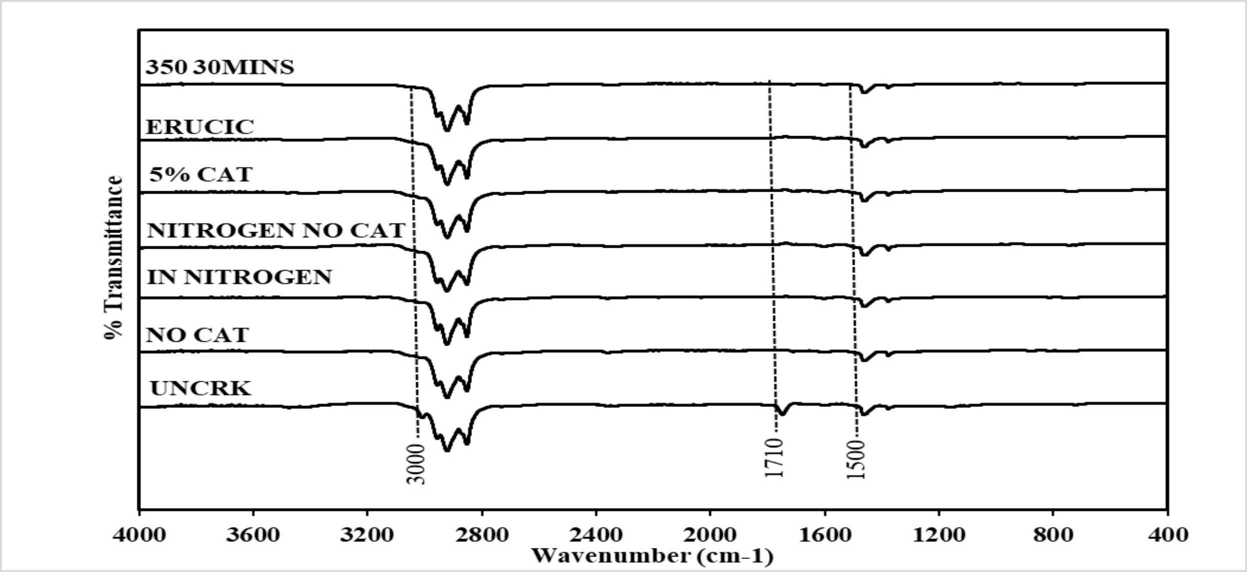


Figure A4.7 FT-IR spectra of HDO oils produced as a result of various process modifications

Table A4.1 Properties of uncracked carnata oil

Properties	Uncracked HEBCO
Composition (wt. %)	
Nitrogen	0.3±0.1
Carbon	70.4±2.1
Hydrogen	11.3±0.0
Sulfur	0.2±0.0
Oxygen	17.9±2.2
HHV (MJ/kg)	36.0±1.0
Water content (wt.%)	N.D.
TAN (mg KOH/g)	N.D.
Density (g/cm^3)	0.9±0.0
Kin. Viscosity (mm^2/s)	43.6±0.0