Experimental Study on Co-processing of Biocrude distillate into Liquefaction Process for Drop-in Biofuel Production

Master Thesis Report

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AALBORG UNIVERSITY
STUDENT REPORT

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Abstract:

Waste-to-energy conversion, especially to high-value transportation fuels is of rising interest. Liquefaction process can transform a wide range of lignocellulosic and biowastes into drop-in bio-crude which is compatible with the existing petroleum infrastructure. This study is dedicated to advancing our understanding of the liquefaction process. Specifically, it aims to investigate an HTL biocrude distillation with a detailed analysis of its fractions. Moreover, it delves into a detailed physical and chemical characterization of bio-crude after liquefaction to evaluate and compare the properties after each treatment, through a different set of experiments using micro-batch reactors. Characterizations such as Carbon, Hydrogen, Nitrogen, Oxygen,HHV, TAN are measured. Additionally, blending potential with petroleum crude oil will be investigated further.

AALBORG UNIVERSITET
STUDENTERRAPPORT

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Titel:
Eksperimentel undersøgelse af sambehandling af biorådestillat i flydendegørelsesprocessen til produktion af drop-in-biobrændstof

Tema:
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Abstract:

Omdannelse af affald til energi, især til højværdi transportbrændstoffer er af stigende interesse. Liquefaction processer kan omdanne proces kan omdanne en bred vifte af lignocellulose- og bioaffald til dråbeformet bio-råolie, som er kompatibel med den eksisterende olieinfrastruktur. Denne undersøgelse er dedikeret til at fremme vores forståelse af flydendegørelse processen. Specifikt har det til formål at in- at undersøge en HTL-biodestillation med en med en detaljeret analyse af dens frak-tioner. Desuden dykker den ned i en de-fysisk og kemisk karakterisering afterisering af bioråolie efter flydendegørelse for at evaluere og sammenligne egenskaberne egenskaber efter hver behandling gennem et andet sæt eksperimenter ved hjælp af mikro-batch reaktorer. Karakteriseringer karakteristika som Carbon,Hydrogen,Nitrogen,Oxygen, HHV og TAN måles. sikret. Derudover vil blandingspotentiale med råolie vil blive undersøgt undersøges yderligere.

Chapter 1

Summary

Fossil fuels have powered the modern world's expansion and progress since the early 20th century, evident in our reliance on natural gas, oil, and coal. However, this reliance comes with significant environmental costs. The combustion of these finite carbon-rich fuels has led to a substantial increase in atmospheric Carbon Dioxide CO_2 and other Greenhouse Gases, such as Nitrous Oxide NO_x), Sulfur gases, and Methane, exacerbating climate change threats. To address this energy problem and reduce our carbon footprint, this thesis focuses on exploring alternative renewable energy sources, specifically through the production and characterization of lignocellulosic bio-crude obtained from a continuous liquefaction system at Aalborg University (AAU).

Lignocellulosic-based bio-crude is a widely used feedstock for upgrading to transportation fuels due to its abundance and renewable nature. The experimental design focused on distilling bio-crude into its fractions and performing further analysis on these fractions. The study employed four different cycle cuts of continuous production, emphasizing the necessity of filtration to remove solids that could adversely affect the treated product.

The solvents used for liquefaction included Tetrahydrofuran (THF) in a ratio of 1:5 and a mixture of Toluene and Isopropanol (Tol/IPA) in a ratio of 1:4:1, under conditions of 350°C for 15 minutes at 60 bar pressure with added nitrogen, along with 10% pure Ethanol by initial weight. The resulting products were filtrated using the same solvent ratios and subsequently analyzed to determine their fuel fraction contributions, elemental composition, Higher Heating Value (HHV), and Total Acid Number (TAN).

Additionally, the thesis presents a theoretical comparison of the feasibility of blending the produced bio-crude with petroleum crude oil to assess its potential for co-processing in maritime fuel production. The findings indicate that, despite improvements in the bio-crude quality, further upgrading is necessary before it can be co-processed in existing refineries.

The conclusion highlights the need for ongoing research and development to enhance the bio-crude upgrading process. Future work suggestions include exploring alternative solvents, optimizing reaction conditions, and integrating advanced filtration techniques to improve the overall efficiency and quality of bio-crude production.

This thesis contributes to the understanding of bio-crude production from lignocellulosic biomass, offering insights into its potential as a sustainable energy source and its integration with existing petroleum infrastructure to produce cleaner transportation fuels.

Preface

This report explores the distillation process of HTL (Hydrothermal Liquefaction) biocrude in detail, including an in-depth investigation of the distilled fractions and an inventive exploration of the method. Central to this investigation is the examination of how these distillate fractions influence the properties of the final oil when recycled back into the liquefaction process using a microbatch reactor system. This study attempts to shed light on the intricate interactions between the quality of liquefaction biocrude oil and the distillation processes through rigorous testing and evaluation. By providing an in-depth physical and chemical characterization of biocrude, the findings presented in this report seek to augment the existing body of knowledge on liquefaction technology, highlighting its potential impacts and efficiencies in the production of biofuels.

Aalborg University, May 31, 2024

Gratitude

The author would like to thank the supervisor Saqib Sohail Toor and co-supervisor Abdenour Achour for their availability, guidance and support throughout the project. She would also like to thank Anette Lund Shmindt and PhD guest Rami Makareem for their collaboration and constant support regarding the analysis equipment calibrations. Lastly, she would like to thank Simon Ruwe for contributing to some of the results presented in this report.

Eleni Maria Boutla

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Abbreviations

NDCs	Nationally Determined Contributions
EU	European Union
IEA	International Energy Agency
HTL	Hydrothermal Liquefaction
HHV	High Heating Value
PAHs	Polycyclic Aromatic Hydrocarbons
GHG	Greenhouse Gas Emissions
HDO	Hydrodeoxygenation
SRGO	Straight Run Gas Oil
SRN	Straight Run Naptha
SRK	Straight Run Kerosene
LPG	Liquefied Petroleum Gas
VGO	Vacuum Gas Oil
FCC	Fluid Catalytic Cracking
H/C	Hydrogen to Carbon
Tol	Toluene
IPA	Isopropanol
Sim-Dist	Simulated Distillation
GC	Gas Chromatography
TAN	Total Acid Number
O/C	Oxygen to Carbon

Symbols

Symbol	*Unit*	*Description*
CO_2		Carbon Dioxide
NO_x		Nitrous Oxide

Gt	Gt	Gigatones
EtOH		Ethanol
MPa	MPa	MegaPascal
C		Carbon
H		Hydrogen
O		Oxygen
N		Nitrogen
S		Sulfur
CO		Carbon Monoxide
THF		Tetrahydrofuran
mL	mL	Milliliter
Min	min	minute
H_2O		Water
MJ	MJ	MegaJoul
Kg	kg	Kilogram
Pa	Pa	Pascal
s	s	second
KOH		Potassium Hydroxide
mg	mg	miligram
C_7		Cycle 7
C_9		Cycle 9
C_11		Cycle 11
C_14		Cycle 14
CH_4		Methane

Chapter 2

Introduction

Fossil fuels have enabled the modern world's great expansion and progress since the turn of the 20^{th} century, as evidenced by our heavy reliance on natural gas, oil and coal. This breakthrough does come with a substantial environmental cost, though. Over time, the burning of the finite carbon-rich fuels has flooded the atmosphere with Carbon Dioxide (CO_2) and other greenhouse gases, including Nitrous oxide (NO_x), Sulfur gases and methane, increasing the grave threat of climate change. It has also resulted in alarmingly high levels of air pollution, putting both ecosystem stability and human health at risk. This conforts a severe environmental catastrophe with consequences including rising sea levels, severe weather and a global decline in biodiversity due to this world's overwhelming dependence on fossil fuels. Urgent action is needed to shift toward cleaner, more sustainable energy sources.[1]

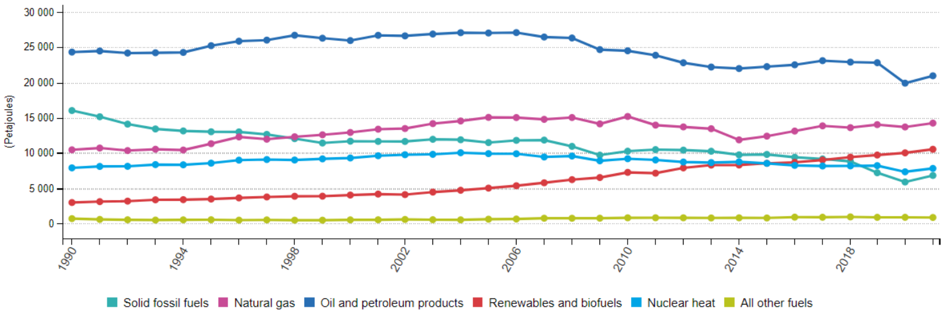

Figure 2.1: Gross available energy dependance in Europe (1990-2021) [2]

Fig 2.1 presents the energy consumption trends from 1990 to 2021 across different energy sources, measured in petajoules. The energy sources include solid fossil fuels, natural gas, oil and petroleum products, renewables and biofuels, nuclear heat, and all other fuels. The graph shows a distinct shift in the patterns of energy usage during the previous thirty years. Traditional energy sources like oil, petroleum, and solid fossil fuels are gradually giving way to more renewable and sustainable energy sources with renewables and biofuels showing a steady increase in consumption throughout the period, reflecting growing investments and policy shifts towards sustainable energy.

In that response, the International community decided in 2015, as part of the Paris Agreement, to keep the rise in global temperature to 2°C for the reference period, with a goal of staying below 1.5°C. This action plan to slow down global warming was ratified by 196 Parties. Among, its principal components are long term goals and strategies as well as Nationally Determined Contributions (NDCs). [3]

More specified, Europe, a major energy consumer, must balance serving the needs of its population and economy for energy with reducing its carbon emissions. The European Union intends to accelerate the use of renewable energy in order to help achieve the targets of reducing greenhouse gas emissions by at least 32% by 2030 and becoming climate neutral by 2050 on the continent. This shift is depicted in Fig2.2 the graph highlights the EU's objective action. Though, The two post-2030 scenarios show divergent directions. To reach a 100% renewable energy system by the middle of the century, the more ambitious scenario calls for radical changes in energy policy, infrastructure, and technology deployment.[2]

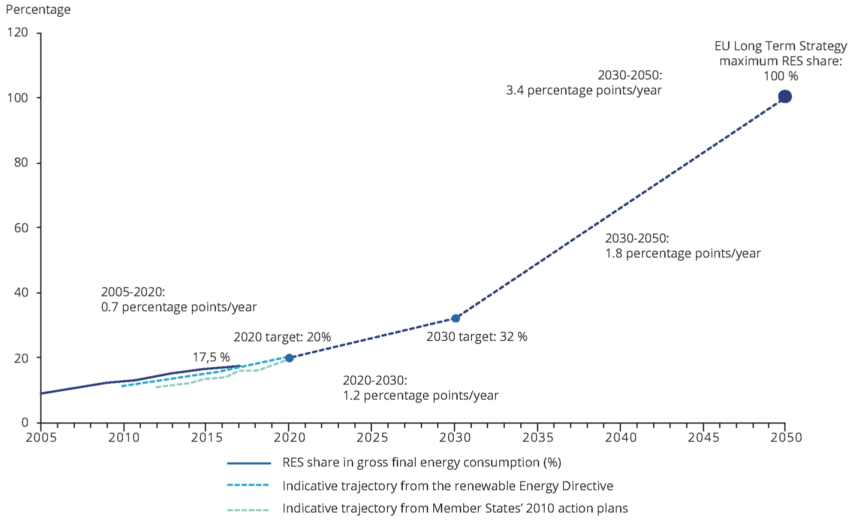

Figure 2.2: Progress towards renewable energy source targets in the European Union [2]

In connection to the transportation sector, approximately 14% of greenhouse gas emissions worldwide are attributed to the transportation industry, which is second only to the power production sector. However, just 2.8% of all bio-diesel used for transportation is produced from renewable sources. Thus, it is expected that the development of new technologies for producing biofuels will reduce reliance on oil and decarbonize transportation, by valorizing the carbon dioxide in the air and creating a closed cycle where the amount of emissions is balanced out by the absorption of CO2 by the biomass. In particular, this is important for heavy transportation, which cannot be easily electrified with the current technologies. According to International Energy Agency projections, when biofuels are produced sustainably, their percentage can increase to 27%, which would result in annual reductions of around 2:1 gigatonnes (Gt) of CO2 emissions. The next generation of biofuels must mature in order to meet this demand. However, in order for these processes to be successfully implemented, they must simultaneously outperform current biofuels while having a noticeably less carbon footprint. Significant political attention has been paid to the development of advanced biofuels, and numerous ongoing initiatives and programs are being carried out globally. For instance, the Horizon 2020 framework provides funding for research initiatives in the field by the European Union. [4] [5] [6]

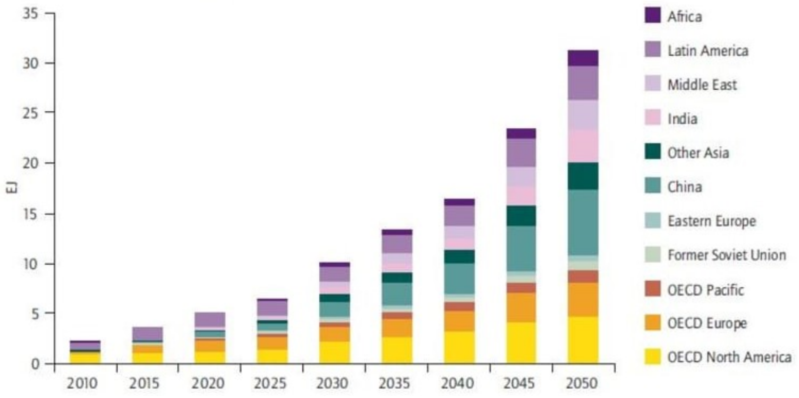

Figure 2.3: Biofuel demand by region 2010-2050
IEAbiofuelroadmap

This report, focuses on the integration of biomass energy into transportation fuels and specifically the maritime sector. Though, in the maritime sector it is not yet possible to utilize renewable energy sources like solar,wind,hydropower, except drop-in biocrude.

HTL or hydrothermal liquefaction is the process of turning biomass into a crude-like oil utilizing different types of feedstocks. Currently, the most researched feedstock are leftover from the other primary human production activities such as agricultural waste, forestry waste, organic municipal waste, etc, and lignocellulosic materials. Thus, waste - to - energy derives from the previous explanation.

This bio-crude cannot be directly refined in the same way as fossil fuel crude oil. The current research is focusing on the different methods of improving bio-crude to optimize the subsequent upgrading operations. To this end, the goal of this research is to use a similar process to HTL known as liquefaction, which is the co-processing of a bio-crude after its solid concentration removal with EtOH additive in order to improve its quality in terms of physical and chemical properties and viscosity. [4] [6]

Chapter 3

Problem Statement

Waste-to-energy conversion, especially to high-value transportation fuels, is of rising interest. Liquefaction process (300°C - 400°C, 10-25 MPa,) can transform a wide range of lignocellulosic and biowastes into drop-in bio-crude which has been defined as functionally equivalent to petroleum-based transportation fuel and is fully compatible with the existing petroleum infrastructure. However, it needs to be further upgrade to drop-in biofuel. The greatest challenges of upgrading biocrude to drop-in biofuel are its poor physical and chemical properties. Biocrude, produced from biomass typically contains high levels of oxygen, nitrogen, and sulfur, along with various contaminants and impurities. These constituents lead to unfavorable characteristics as elevated acidity, elevated viscosity, and instability, rendering the biocrude unfit for direct application in the current fuel infrastructure.

In this project, the following topics will be investigated in detail:

- Distillation of HTL biocrude and analysis of the distillation fractions.
- Investigation of the effect of distillate fractions on the final oil properties after recycling it into HTL process using microbatch reactor system.
- Detailed physical and chemical characterization of biocrude.

With all this at hand, the main objective of this thesis project is to answer the following research questions:

- What would be the effect of solid removal in earlier cycles?
- Are the properties of the bio-crude better after liquefaction?

Chapter 4

Biomass feedstocks, Conversion Methods and Bio-crude Composition

4.1 Biomass feedstocks and conversion methods

Biomass is defined as energy obtained from live or recently living organisms. In order to produce heat, mechanical energy, electricity (bio-energy) and biofuels, biogenic materials originating from agricultural crops, residues, forest products, aquatic plants, manures, and wastes can be burned directly or after conversion processes which will be further analyzed. Many nations encourage increased use of bioenergy as a way to cut back on greenhouse gas emissions, reliance on imports, and the use of non-renewable energy sources like fossil fuels.One straightforward method is direct combustion, where biomass is burned to generate heat or electricity. As an alternative, biomass can be processed by turning it into a liquid by using techniques like rapid pyrolysis or hydrothermal liquefaction (HTL). These techniques convert the biomass's complex organic components into an oil that resembles crude, which can then be processed further to produce biofuels and other useful compounds. This strategy contributes to a more sustainable and financially feasible energy system by making energy more adaptable and portable and by enabling the creation of a larger range of end products. The conversion of biomass to liquid or gaseous fuels by chemical and/or physical means is of great interest since the transportation sectors need such fuels. Biocrude may be refined and processed to create a variety of transportation fuels that can be used in current cars with little to no engine and fuel system modifications. [7]

4.1.1 Biomass feedstocks and categories

Biofuels are generated from biomass, a renewable energy source. The moisture content, heteroatom composition, bulk density, particle size/shape distributions, and other properties of biomass will directly affect the conversion method and the final composition of the biofuel. Based on the feedstock and the production method biomass can be derived in four generations: first, second, third and fourth. [7]

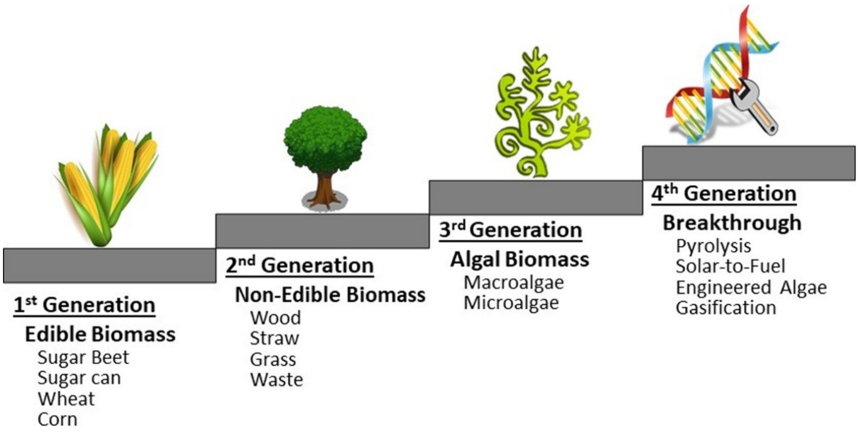

Figure 4.1: Generations of biomass
[7]

More analytically, first generation biomass is constituted by food crops cultivated on arable land, such as corn, sugar, starch, and grains. Though, since there is a counteraction between the food and fuel industry, utilization of first-generation biomass in the manufacture of biofuel is controversial. The lower socioeconomic strata may suffer grave societal repercussions if food prices rise as a result of this rivalry. The creation of biogas, biodiesel, syngas, and other products is the outcome of mostly biochemical conversion processes in this generation. Owing to the aforementioned dispute, researchers began concentrating on second-generation biomass, or feedstocks from non-food crops. An example of first generation biomass could be sugar acne. It has shown promise for the future since it produces biofuel, such as ethanol, which is frequently used in low-level blends with transportation fuel. This method primarily uses biochemical conversion, in which sugar cane is crushed in water to separate the sugars from bagasse, which is then burned to provide heat or power. After the sugar's impurities are eliminated, it goes through a fermentation process to produce CO_2 and ethanol. Conversion methods will be discussed further on the report. Moreover, this generation posses a significant role in the industrial evolution since the technology utilized is already known. On the other hand, as mentioned earlier it competes with food industry and potentially leading to price increases and land use. [7] [8] [9]

The two primary categories of second-generation biomass are lignocellulosic biomass and organic waste, which includes manure and sewage sludge. This generation is more interested in using thermochemical processes, such as pyrolysis or HTL. The advantages of them consist of the utilization of non-food biomass and wet-biomass. However, they are still primarily in the pilot stages thus needing more advancements to be price competitive contrary to the first generation biomass. Hemicellulose which is mostly consisted of plant matter and is utilized extensively in the paper industry, has a lot of promise for being converted into biofuels. The quality of the biomass is mostly determined by the structure of the plant and is primarily structured of cellulose, hemicellulose, and lignin, with trace amounts of pectins, proteins, and other substances. [7] [8] [9]

Third-generation biomass refers to feedstocks, such algae and duckweed, that have a higher energy density per harvest area than first- and second-generation biomass. Approximately 80% of the biomass produced by algae contains lipids, which can be extracted and used into fuel. Additionally, this feedstock is well-known for growing swiftly on less area and for using CO_2 as feed through photosynthesis. More analytically, algae is an aquatic photosynthetic organism that utilizes sunlight and CO_2 to make energy. Because of the high lipid content in this biomass, ethanol can be generated from it. This resource's primary benefits are its quick growth rate, low area requirements, and high photosynthetic efficiency. The primary issue is how much it costs to harvest and how much water is needed in order to produce it. It is estimated that 90% of the equipment costs for producing open-pound algae are related to harvesting and dewatering. Its high water content makes it ideal for thermochemical reactions like HTL, which call for a moist reaction environment. [7] [8] [9]

Lastly, referring to the fourth generation biomass genetically modified organisms are used, which may also incorporate carbon capture and storage. Through genetic engineering, this generation hopes to increase the sustainability and efficiency of biofuel production. Plants and microalgae that have undergone genetic modification are designed to produce more hydrocarbons or fats, or to excrete fuels that are ready for use. A few benefits include the possibility for significantly higher yields of biofuel and photosynthetic efficiency, as well as the potential to absorb more CO_2 during combustion than biofuel does, particularly when paired with carbon capture systems. However, there are strict approval processes and public scrutiny for genetically modified organisms in agricultural and energy production. Not to mention, there is a chance that unintentional releases of genetically modified animals into the wild could have unforeseen ecological effects. [7] [8] [9]

4.1.2 Biomass conversion methods

Biomass conversion methods are essential techniques for raw biomass to be converted into useful energy sources like heat, electricity and biofuels. Figure 4.2 portrays the biomass conversion methods and their products.

The two basic mechanisms that turn biomass into biofuels are thermochemical

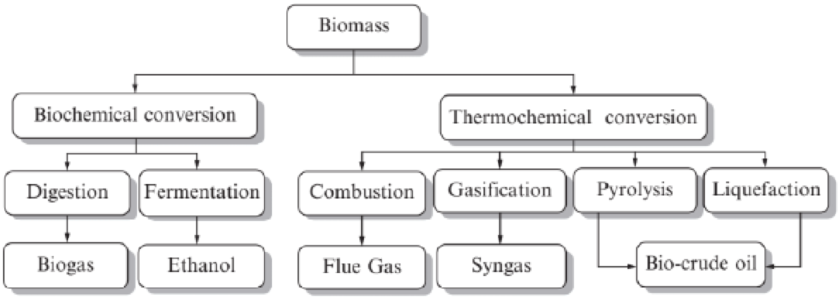

Figure 4.2: Biomass conversion methods
[10]

and biochemical. As illustrated above, biochemical conversion can be consisted of Digestion and Fermentation with Biogas and Ethanol as their products respectively. Thermochemical conversion is considered the most important part of biomass conversion for fuel transportation production. This is a result of their capacity to convert biomass into liquid fuels with a high energy content that are compatible with the fuel infrastructure already in place and can satisfy the demanding energy needs of the transportation industry, which includes the road, aviation, and maritime sectors. More analytically, they are divided to Combustion, Gasification, Pyrolysis and Liquefaction with their products being Flue gas, Syngas and Bio-crude oil respectively. [2] [11]

This report will focus on paths for maritime transportation fuels and mainly liquefaction.

4.1.3 Liquefaction

Liquefaction can be derived as an effective thermochemical method for turning biomass into charcoal, gases, and the desired product (bio-crude). The procedure is typically performed at 250-400°C and 5-25 MPa in water or another appropriate solvent. It is considered to encompass processes like Hydrothermal Liquefaction (HTL). In the context of this report, pyrolysis will not be described since it is not a relative biomass conversion method. However, HTL will be described in the following subsection. [11]

Hydrothermal Liquefaction

Hydrothermal Liquefaction (HTL), also known as hydrous pyrolysis, is a thermochemical depolymerization process in an enclosed reactor to transform wet biomass into bio-crude oil and chemicals under moderate temperature (usually 200-400°C) and high pressure usually (5-30MPa). Under these circumstances, a range of physical and chemical processes are applied to the organic components, yielding four distinct products: gas phase, biocrude, aqueous phase, and solid phase. [12] Figure 4.3 shows a simple HTL and its obtained products.

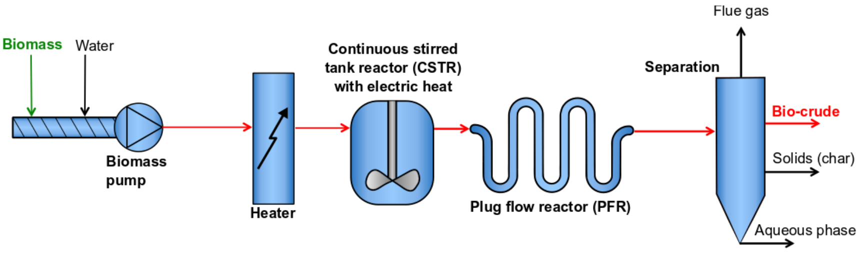

Figure 4.3: HTL biomass process scheme and its products [12]

HTL biocrude is a more promising technology since it has a lower oxygen content—roughly 10%—than pyrolysis, which produces a 40%–50% oxygen content. It also has a lower water content and other advantageous features to generate drop-in biofuels. Depending on the treatment parameters and the chemical composition of the biomass, HTL biocrude exhibits yields ranging from 20 to 50 percent. Since the biocrude cannot be used directly due to its high viscosity, low HHV, heteroatom presence and poor thermal stability, it still needs to be enhanced through hydroprocessing. [12] [13] [14]

4.2 Biocrude composition depending on the feedstock

The composition of biocrude produced from biomass varies significantly depending on the type of feedstock used, which is intrinsically linked to the elemental composition of the biomass. [11] Biomass is primarily composed of carbon (C), hydrogen (H), and oxygen (O), with smaller amounts of nitrogen (N), sulfur (S), and other elements. These elemental constituents play a critical role in determining the chemical makeup and properties of the resulting biocrude. The most important component is Carbon, which is obtained from atmospheric CO_2 during photosynthesis and can burn to produce CO2 as well as possibly form contaminants such carbon monoxide and PAHs. Phenolic and carbohydrate polymers contain hydrogen; woody biomass contains 6-8% of hydrogen while herbaceous biomass has 5.5–6%. Fertilized herbaceous biomass has increased levels of nitrogen, which is necessary for plant growth and speeds up biological processes. Proteins contain sulfur, which is also essential for growth. Herbaceous crops have higher levels of sulfur (0-0.2%) than woody biomass (up to 0.1%), and larger levels of sulfur in waste fractions have an impact on emissions and corrosion. Even while oxygen is essential, its difficult removal from phenolic compounds limits the usage of biocrude. [11] [15] [16] [17]

HTL biomass will undergo three basic steps: [11]

- Hydrolysis of the complex organic molecules into simpler compounds under high temperature and presence conditions.
- Depolymerization of the long structure chains of polymers into shorter chains.
- Decomposition step involving dehydration, decarboxylation and deammination,forming water soluble compounds and gases.
- Repolymerization of the reactive substances into solids.

Different biomass types will undergo different reactions which will eventually lead to the formation of the biocrude. More analytically the feedstocks are displayed below.

Cellulose

Cellulose is the most abundant organic compound on earth with a chemical formula of $(C_6H_10O_5)_n$. It is a complex carbohydrate consisting of oxygen, carbon, and hydrogen. It is chiral, tasteless and has no odour with a high molecular weight and high polymerization order. [18] [19] [11]

Its formation stands by the connection from glucose molecules to D-anhydroglucopyranose units with (1 - 4)-/β-D-glycosidic ether bridges. Its structure is presented at 4.4. Cellulose has a rigid structure solely due to its strong intramolecular hydrogen bonding.

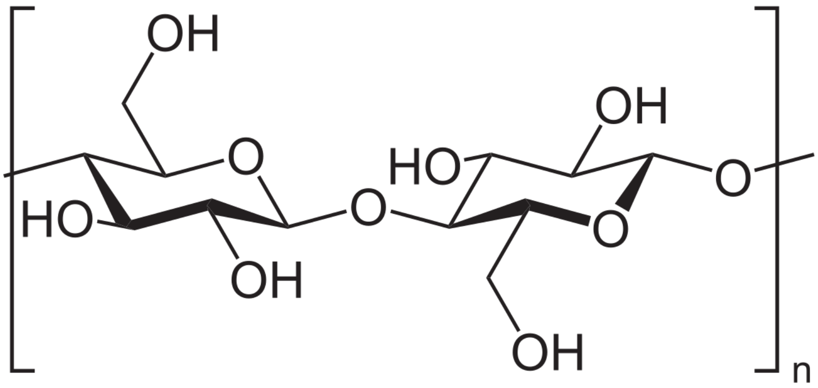

Figure 4.4: Chemical formula of cellulose
[19]

Hemicellulose

Hemicellulose is a branching polymer divided into numerous pentoses and hexoses. In contrast to cellulose, hemicellulose has less hydrogen bond stabilizers, which facilitates the polymers' simpler breakdown. Galactose, pentoses, mannose, and glucose often make up the major chains of hemicellulose. The side chains consist of functional groups including acetic acid, pentose, hexoses, heruronic acids, and deoxyhexoses that are in charge of the hemicellulose's solubility in the aqueous phase. [20] [21] Figure 4.5 represents a Hemicellulose composition in hardwood.

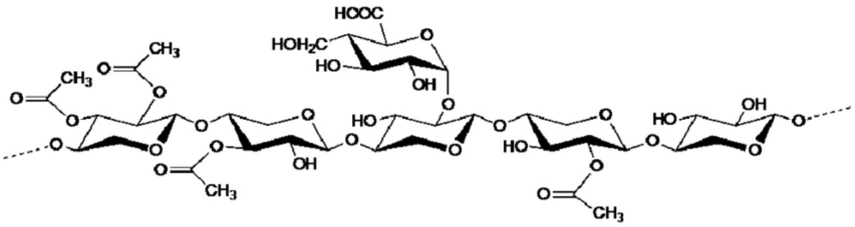

Figure 4.5: Hemicellulose composition in hardwood
[20]

Lignin

Lignin is defined as a complex organic polymer containing oxygen which comprises up the majority of wood together with cellulose. It is the second most prevalent organic material on Earth after cellulose, yet there aren't many industrial use for it outside from fuel production. Often referred to as an aromatic chemical, it is composed of up of hydroxyl groups attached to phenyl-propane by ether bonds and ethoxy groups. All lignins are composed of three basic building blocks: trans-p-coumarlyl alcohol, coniferyl alcohol, and sinapyl alcohol. Lignin has a structure that is cross-linked and complicated, making it extremely resistant to breakdown.Since lignin has a higher energy content than the other two ingredients, the products have a higher heating value. [22] [18] [11] Figure 4.6 represents a simple lignin structure.

Lipids

Lipids are defined by a large group of compounds which includes fats, waxes, sterols, fat-soluble vitamins (such as vitamins A, D, E and K), monoglycerides, diglycerides, phospholipids, and others. At atmospheric temperature these compounds are non-polar, but as the temperature rises they incline to polarization. [24] [25]

Proteins

Proteins are a significant component of many biomass feedstocks; they are mostly present in food crops, algae, organic waste, and minor amounts of lignocellulosic biomass. Amino acid polymers make up proteins, which also contain peptide bonds—amide bonds between carboxyl and amine groups—that bind amino acids together. Because of their strong connections and tremendous complexity, amino acids are difficult to degrade. .[18] [11]

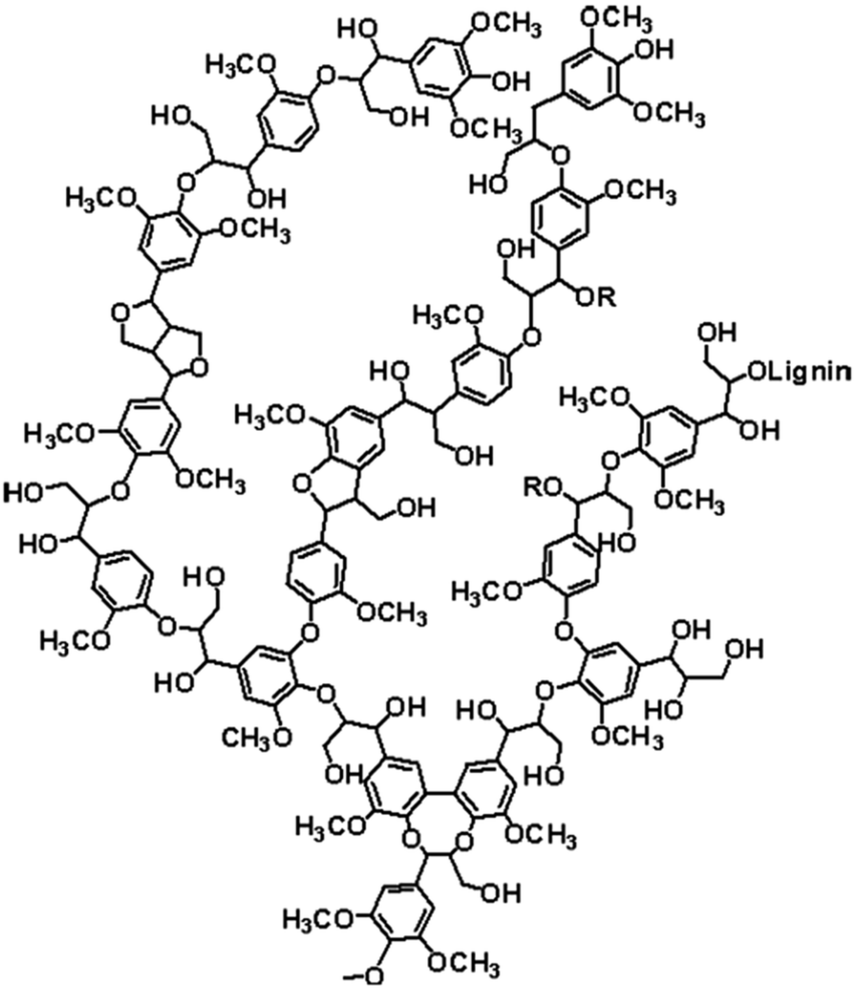

Figure 4.6: Lignin structure
[23]

4.3 Drop-in Biofuels

The maritime sector is responsible for 2.8% of the worldwide GHG emissions with agencies trying to reduce this environmental impact. Drop-in biofuels represent a significant advancement in the quest for sustainable and renewable energy sources. Also, they are designed to be fully compatible with current petroleum-based fuel systems. Acoording to IEA (International Energy Agency): "Drop-in biofuels are liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure".

This indicates that drop-in biofuels are renewable fuels that may be utilized in the present petroleum refinery infrastructure, including pipes, pumps, and other

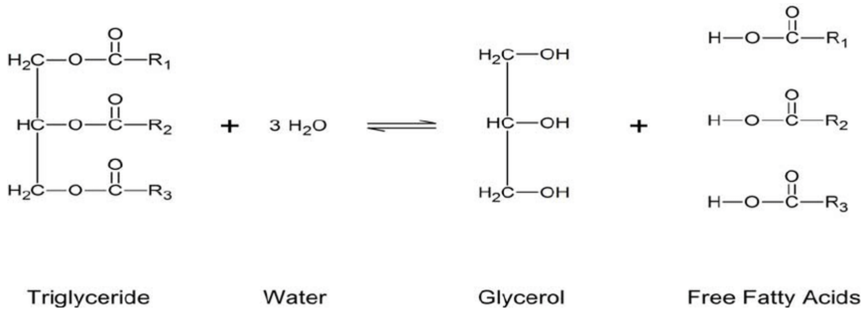

Figure 4.7: Hydrolysis of triglycerides
[24]

equipment, as well as combined with products made from crude oil. [26] [27]

4.4 Potential of integrating biocrude into existing refineries

The integration of biocrude into existing petroleum refineries, known as co-processing, offers a promising pathway to increase the production of renewable fuels while leveraging the established infrastructure and technological capabilities of the petroleum industry. Co-processing involves blending biocrude with traditional petroleum feedstocks and processing them together in conventional refinery units. This approach helps mitigate some of the challenges associated with biocrude upgrading and supports the transition to more sustainable energy sources. Hydrotreatment of the biocrude prior to co-processing is necessary in order to meet conventional petroleum standards before introducing it in the refinery streams since refineries are optimized to the specific crude feed as well as the targeted market. This is important because refineries are designed to be compatible and efficient in the refining process by being optimized for particular crude inputs and target markets. Utilizing milder hydrotreating operating conditions, which lowers process costs, and eliminating all medium to high HDO reactivity oxygenates to enable co-processing at an existing refinery are the optimal results to increase the co-processing compatibility of biocrude. The low HDO reactivity oxygenates, which are probably found in the residue fraction, would be the only oxygenates left. These oxygenates need severe process conditions and use a lot of hydrogen. The residual heteroatoms could be eliminated and the boiling point could be lowered by cracking reactions in refineries using robust process units to convert these oxygenates. The primary concept is that the hydrotreating process's operating parameters can be changed to modify the characteristics of the final product and produce improved bio-oils that are suitable with co-processing or drop-in biofuels. [28] [13]

Nowadays, it is not feasible to build refineries that are only focused on producing biofuels because of time-consuming logistical problems and financial considerations that call for a substantial initial outlay. Using currently operating petroleum refineries to carry out a portion of the production process of biofuels is a far more practical solution in the short run. Because it reduces production costs, co-processing biocrude at current refineries is thought to be a very promising way to obtain drop-in biofuels in the market. In order to gain a deeper understanding of the process, a closer examination of the traditional petroleum refinery is necessary. Among other metrics and features, the goal is to investigate potential sites for biocrude insertion. These procedures, which fall into the categories of separation and conversion, are as follows: [29] [30] [13] [28]

Separation processes

- **Atmospheric Distillation:** Desalted crude oil is separated into multiple fractions based on their respective boiling points through an atmospheric distillation unit. The end products include residue, straight-run gas oil (SRGO), straight-run naphtha (SRN), straight-run kerosene (SRK), and liquefied petroleum gas (LPG). We refer to these as straight-run products.
- **Vacuum Distillation:** The atmospheric residue is separated under vacuum conditions (reduced pressure leads to lower boiling points), producing vacuum gas oil (VGO) and vacuum residue.

These separation processes will be explained further in this report.

Conversion processes

- **Hydrotreating:** Utilizes Hydrogen as a reactant to remove or reduce unwanted oxygen, sulfur and nitrogen.
- **Reforming:** Transforms desulfurized naphtha molecules into molecules with a higher octane to create reformate, a constituent of gasoline. One important byproduct that is extracted from the reformate is hydrogen.
- **Isomerization:** Transforms linear molecules into higher octane molecules so they can be mixed with gasoline.
- **Hydrocracking:** Heavy oil fractions are cracked to create lighter, more valuable, decreased viscosity products with lower boiling points when catalyst and hydrogen are present.
- **Fluid Catalytic Cracking:** Catalytic cracking of heavy oil fractions results in lighter products with lower boiling points. The primary driving force for catalytic cracking is the requirement to produce more gasoline.
- **Coking:** Very heavy residual oils are severely thermally cracked, producing gasoline and diesel fuel as byproducts, with solid coke remaining.

4.4.1 Insertion points of co-processing of biocrude in existing refineries

Insertion points in already existing refineries are crucial for the effective co-processing of bio-crude, as explained in the previous section. These insertion points determine how biocrude is integrated into the refinery's processing streams, impacting both the efficiency of the conversion process and the quality of the final fuel products.Figure 4.8 represents the possible insertion points of bio-crude co-processing in already existing refineries.

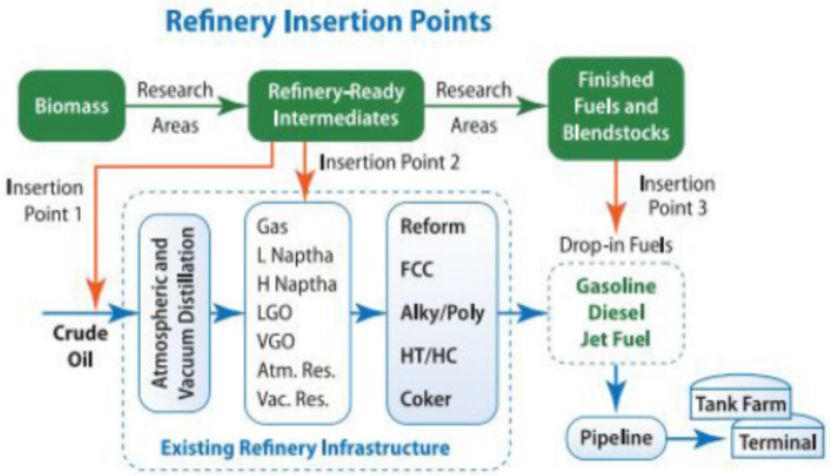

Figure 4.8: Insertion points for co-processing in already existing refinery industry [31]

As depicted, three primary insertion points have been identified. The first insertion point provides the best case scenario for co-processing, but it also carries the most risk for the refinery. Contaminants in the imported bio-oil run the risk of spreading throughout the entire refinery. At this point, the biocrude needs to be almost completely devoid of impurities, oxygen, alkanes and reactive oxygenates. Heteroatom distribution is another factor to take into account. In crude oil, these are more equally distributed over all boiling fractions, while in HTL biocrude, they rise with boiling point. At this point of insertion, it must be possible to combine petroleum and upgraded biocrude since the heteroatom distribution in the biocrude needs to be very similar to that of crude oil. The second insertion point delves into the potential integration of bio-oil into intermediate refinery operations. In this case, the bio-product is frequently added either before to the hydrocracking step or the Fluid Catalytic Cracking (FCC) unit. This strategy isn't the best though, as enhanced HTL biocrude is too valuable to mix with air distillation byproduct. Furthermore, there are more hazards at this insertion point because hydrocracking reactors are extremely sensitive to oxygen levels, which could result in catalyst contamination and other problems for the refinery. Lastly, the third insertion point It's intended for drop-in finished biofuels. This indicates that the biocrude has undergone full hydrotreatment and is ready for use in petroleum-powered engines. As shown, these fully improved biocrudes are usually used as blendstocks with other petroleum refinery products. Since biofuels are typically supplied as fully developed, transportation fuels. [28] [31] [32]

4.5 Fuel Boiling Points

Crude oil is a complex mixture of several hydrocarbons that has been tainted over time by other undesirable substances like metals, nitrogen, sulfur, and oxygen. Since hydrogen and carbon constitute the majority of crude oil, the ratio of hydrogen to carbon influences the physical characteristics of the oil. The hydrocarbon's boiling point will be greater if the H/C ratio is low. As a result, the hydrocarbons are divided into various groups according to the ranges of their boiling points. These hydrocarbon groups are separated into various fractions and then given particular treatments to produce the desired final product. After being separated into various fractions, these hydrocarbon groups go through a particular process to produce the intended final product. [33] [34]

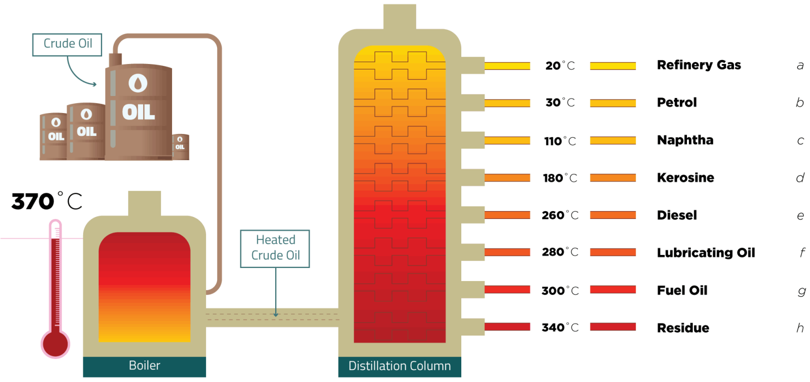

Figure 4.9: Different boiling point for each hydrocarbon fraction.

[33]

Figure 4.9 represents the different boiling points for each hydrocarbon fraction. Liquefied petroleum gas (LPG), which is mostly made up of butane, propane, and ethane and usually contains hydrocarbons with one to four carbon atoms, has the lowest boiling point and the lowest carbon number. Octane levels, which indicate how resistant gasoline is to autoignition in spark-ignition engines, are used to classify gasoline. Higher octane levels are associated with higher gasoline ratings, and gasoline is composed of hydrocarbons with four to twelve carbon atoms per molecule. The primary limiting factor in jet fuel, which is manufactured in accordance with international standards, is its freezing point. Depending on whether it is naphtha- or kerosene-type jet fuel, the carbon number can range from 5 to 16. Diesel usually uses compression-ignition engines and ranges from 30 to 60% cetane. The cetane number is used to express the volume percentage of cetane in the mixture. Usually utilized for heat generating, heavy fuel oil is made up of long hydrocarbon chains and aromatics, with each molecule having nine to seventy carbon atoms. Remainders from distillation are used to make asphalt, a crucial ingredient for the building sector, as well as other goods like waxes and lubricants. [33] [34]

In connection to conventional crude oil boiling points, bio-crude shares the same complex characteristics and need to meet specific characteristics in order to be utilized as a fuel. [35]

4.6 State of the Art

This State of the Art section provides a brief review of the advancements in liquefaction investigating different parameters, feedstocks and co-solvents.

Barnes et al. [36] conducted a liquefaction experiment with pine wood as feedstock in different solvents. The liquefaction experiments were executed in a 45mL autoclave made of Inconel 825 and equipped with a mechanical stirrer. In all experiments, 10% wt of dry biomass and 90% wt of solvent were introduced into the reactor. The experiments were performed at 310°C for 30 min.The collection of solvents comprised anisols, phenolics, and paraffinic and aromatic hydrocarbons. Using different solvents produced there was a broad variety of product yields production. Paraffinic solvents typically produced the highest production of char, followed by aromatics, anisols, and phenols. On the other hand, the experiments conducted with a mix of solvents indicated the lowest solid yields. All in all, throughout their experiments they concluded that the biocrude was soluble in all of the solvents that were taken into consideration. Protic solvents cause the wood conversion rate to decrease, while water increases it. Therefore, longer reaction durations may be necessary for protic solvents to completely liquefy. In general, the char production of aromatic solvents is reduced by the addition of water or phenols. During liquefaction, phenolic solvents have a tendency to break down and mix into the distillate portion of the biocrude.

Another study conducted by Bulutcem et al. [28] where they liquefied oak wood using various solvents for Bio-oil production. In their study they performed the experiments in a 300 mL pressurized and stirred batch reactor that was equipped with an adjusted cooler and heater to retain the desired operating temperature. Before all experiments, pure N_2 was used to purge the inside of the reactor from gases and for each run, 4 g of OWP was loaded with 100 mL of a pure solvent. The solvents used were water, ethanol, 1-butanol, and 1,4-dioxane. The experiments were conducted in different temperatures ranging at 210°C, 240°C and 270°C for 1 and 2 hours. After the reaction they followed separation process. This research indicated that the most beneficial reaction time would be 1h, at 270°C. 1,4-Dioxane, showed the best performance in producing liquid products at 52.2% as well as bio-oil yields at 51.8%. HHV of the oils ranged from 22.1 to 35 MJ/kg with the best solvent being 1-butanol for this analysis. Finally, the elemental analysis designated that the Carbon was much higher whilst the Oxygen much lower to the initial feedstock with the H/C ratio of ethanol being the lowest.

Chapter 5

Methods and Materials

The experiments were conducted at the Biofuel Production Lab of AAU. The bio-crude used in this study has been obtained from the processing of lignocellulosic biomass with solvent in a continuous pilot at Aalborg University.

5.1 Experimental Procedure

The continuous liquefaction system at AAU offers and advanced approach to converting biomass into bio-crude.

Delving into the continuous system regarding this project's experimental work it is essential to analyze further the process regarding the production of the bio-crude that has been used. More analytically, the process begins with the introduction of pine wood biomass and ethanol into a blending tanker. The pine wood is finely ground to ensure uniformity and optimal reaction surface area. Ethanol is added to the tanker, and the mixture is thoroughly blended to create a homogenous feedstock slurry. The blended feedstock is then transferred to a reaction tanker where the hydrothermal liquefaction process occurs. In this reactor, the mixture is subjected to high temperatures and high pressures to facilitate the breakdown of biomass into biocrude. The system is designed to recycle the biocrude for further refinement. After each HTL cycle, light fractions are trapped in a designated flask, and the produced biocrude is returned to the initial blending tanker. This recycling process enhances the conversion efficiency and quality of the bio-crude. In this study, the recycling process was repeated for 14 cycles. The bio-crude that is recycled through the system undergoes multiple refining stages. After the completion of each cycle, the final bio-crude product is collected for comprehensive analysis.

For the scope of this project samples were obtained after C_7, C_9, C_{11}, and C_{14}. The objective behind this is to compare the physical and chemical properties of each cycle and try to optimize them. After C_{14} , the bio-crude produced was subjected to fractional distillation in the laboratory to separate it into distinct boiling point fractions. This step is crucial for understanding the composition and potential applications of the bio-crude components. The bio-crude was heated, and the resulting vapors were condensed and collected in separate fractions based on their boiling points.

Analysis was conducted that will be further discussed through this report.

Following the successful completion of the initial 14 cycles HTL and subsequent distillation of the bio-crude, further experiments were conducted to refine the process and explore different operational conditions. These experiments focused on the liquefaction of bio-crude with removed solids for samples of the cycles chosen. Therefore, these cycles were prepared with solid removal with Tetrahydrofuran (THF) with a ratio of (1:5) where one gram of bio-crude sample was dissolved with 5 grams of THF, as well as a mixture of Toluene/IPA in a ratio of (1:4:1) respectively. These cycles showed the most potential for separating the bio-crude by its respective solids. After the solid removal, the solids were collected in a filter and dried overnight in the oven at 60°C, whilst the sample was put in the rotary evaporator for solvent extraction. Thus, the sample collected was mixed with EtOH, pressurized with nitrogen, and liquefied in a micro-batch reactor at 350°C for 15 min and then cooled down to finalize the reaction for a further 15 min. The experimental setup configuration is depicted in the following table for further understanding.

Table 5.1: Experimental Setup Configuration

Cycle	Solvent for solid extraction	Ratio of solvent	Solvent added
7	THF	1:5	10% EtOH
7	Tol/IPA	(1:4:1)	10% EtOH
9	THF	1:5	10% EtOH
9	Tol/IPA	(1:4:1)	10% EtOH
11	THF	1:5	10% EtOH
11	Tol/IPA	(1:4:1)	10% EtOH
14	THF	1:5	10% EtOH
11	Tol/IPA	(1:4:1)	10% EtOH

The experimental procedures followed are shown in 5.1 and 5.2.

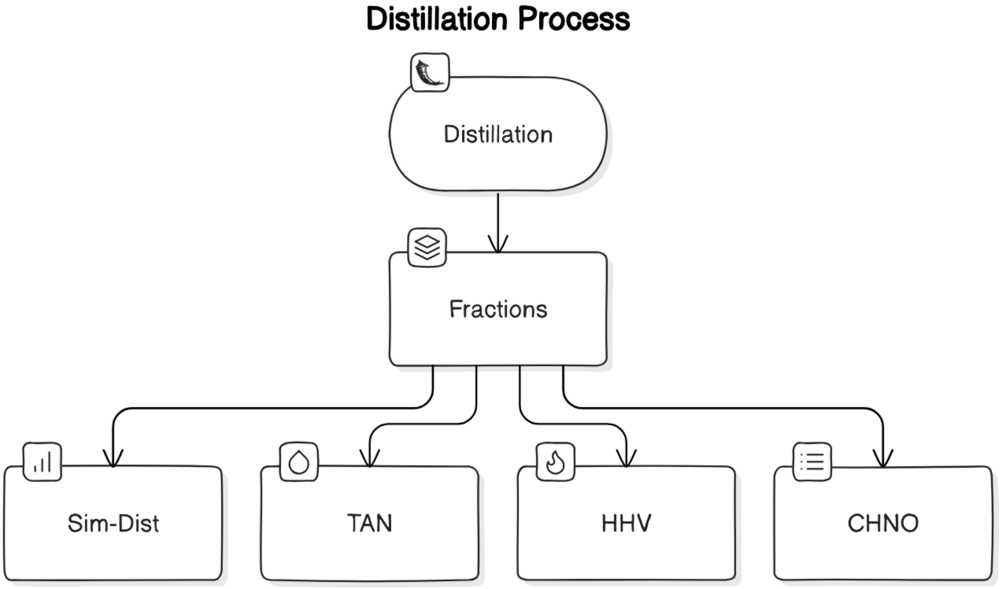

Figure 5.1: Experimental Procedure for Distillation

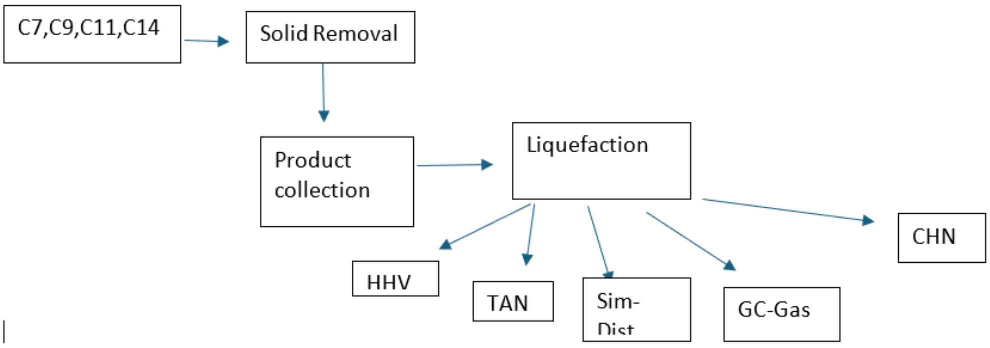

Figure 5.2: Experimental Procedure for Liquefaction

5.2 Feed characterization

This section provides an insight to the biocrude characterization. Figure 5.3 illustrates the bio-crude that was used for the experiments. More specifically it is obtained from cycle 14.

Figure 5.3: Biocrude utilized for the experiments

Table 5.2: Elemental Composition of cycle cuts together with water content, HHV, ash content.All on wt% dry basis

Cycle	Water content	C	H	N	O	HHV	Ash content
C_7	1.619	78.74	9.05	0.45	13.41	35.73	
C_9	0.844	82.61	8.64	0.31	9.29	35.18	
$C_1$1	1.690	78.14	8.54	0.52	14.52	34.51	
$C_1$4	2.136	78.26	8.00	0.27	15.66	34.24	0.2

The elemental analysis (CHNS) of biocrude was performed with a 2400 Series II CHNS/O Element analyzer (PerkinElmer,USA). TocoPhenol Nikotine was used as a calibration standard. Carbon, nitrogen, hydrogen and oxygen were calculated whilst sulphur was not detected with this method. These results are depicted in the table above.

The estimation of HHV was made by the Bomb Calorimeter IKA C2000 Basic,whilst the water content was measured with the TitroLine 7500 basic unit. Lastly, ash content was determined by incineration at 775 °C and measuring the mass of the remaining products afterwards.

5.3 Experimental setup

The experimental setup will first be described by the distillation column and after with the micro-batch reactors and an overview of the sand-bath system.

5.3.1 Distillation Column

The distillation column used at AAU Production lab is depicted at 5.4.

Figure 5.4: Distillation Unit at AAU

5.3.2 Experimental Setup for micro-batch reactors and sand bath

The experimental setup comprises of two 5-15mL micro-batch reactors, a fluidized sand bath, a shaking apparatus to enhance reactant mixing, pressure transducers for each reactor, as well as temperature and air flow controllers. The process is depicted at Figure 5.5

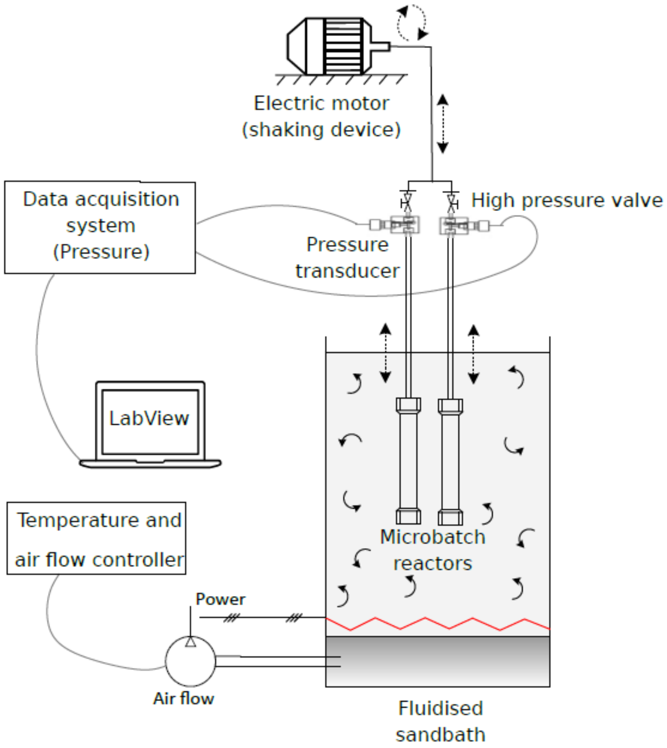

Figure 5.5: Schematic diagram of experimental setup.
[37]

5.3.3 Microbatch reactors

The scope of this research is to examine the influence of different parameters in the biocrude. In that case, two micro batch reactors were chosen as a better option. A clamp is needed to secure the reactors to the agitating device. The top portion of the reactors has a valve for extracting the gases, a pressure transducer for assessing the pressure profile inside the reactors, and others.

An SBL-2D fluidized sand-bath (Techne, Stone, UK) was used to heat the reactors to the appropriate temperature. Reactors heat up more quickly when there is improved heat transfer from the sand acting like a fluid (fluidization). There is only one temperature control in the sand bath. To guarantee effective sand fluidization, the air flow is manually adjusted. An A-10 pressure transducer (Wika, Klingenberg, Germany) was used to continually measure the pressure inside the reactors. A LabVIEW application was used to record and analyze the pressure profiles.

5.4 Experimental procedure

The experimental procedure followed will be described below.

Two microbatch reactors were filled with 3.5 g of biocrude oil and 0.5 g of pure ethanol. The reactors are sealed, pressured with nitrogen, and submerged in water to check for potential bubbles (leaks). At the appropriate pressure (60 bar), nitrogen is added to the reactor if no leaks are found to initiate faster the reaction. The pressure temperature is obtained by connecting the prepared reactors to the pressure transducer. Next, the reactors are affixed to the agitating apparatus and submerged in the sand bath at 350°C. The reactors are removed from the sand bath and submerged in water to cool for fifteen minutes once the targeted residence time of fifteen minutes has been reached. After cooling down, the gaseous products are collected before opening the reactor and extract the liquid products for further analysis. Lastly, the reactors were thoroughly clean to ensure that no residue remained and avoid possible contamination in future experiments.

5.5 Product analysis

5.5.1 Gas phase analysis

The amount of gas produced was calculated by comparing the mass before and after the reactors were vented. A Shimadzu gas chromatograph model GC-2010 with a barrier ionization discharge (BID) detector was used to evaluate the gaseous products after they were collected in gas traps. Each component of the mixture was separated using a fused silica capillary column. The carrier gas used for the study was helium (15 mL/min).

5.5.2 Elemental analysis of liquid phase

The elemental analysis (CHNS) of biomass and biocrude was performed with a 2400 Series II CHNS/O Element analyzer (PerkinElmer,USA). Coco Nicotine was used as a calibration standard. The carbon, hydrogen nitrogen and oxygen was determined whereas in some cases that will be stated oxygen was calculated by difference. Sulphur was not detected by this method.

5.5.3 Simulated Distillation (Sim-Dist)

Simulated distillation is a GC method that allows to quickly characterize fractions within the oil according to their boiling point distribution. It is especially helpful for microscale parametric research, where a small sample size may make conventional distillation challenging. When examining bio-crude materials, one must be mindful of the method's limitations. This is because, although bio-crude oils could also contain other atoms, the calibration is carried out using a pure hydrocarbon standard. This has an impact on molecular weight, which may not be consistent with the relationship between the weight of the standard and the chromatograph signal. This analysis was conducted in a Gas-chromatograph GC-2010 by Shimadzu.

5.5.4 Karl Fischer

After liquefaction in high temperatures there is H_2O production. The purpose of this procedure is to determine the water content of a sample. The analysis was conducted in a TitroLine 7500 basic unit, with Interchangeable dosing unit WA20ml.

5.5.5 Total Acid Number (TAN)

The purpose of the procedure is to determine the Total Acid Number (TAN) of the biocrude samples before and after liquefaction. TAN is a measurement of acidity that is determined by the amount of potassium hydroxide that is needed to neutralize the acids in the oil sample.

5.5.6 Viscosity

The purpose of this procedure is to determine the viscotiy of liquid samples. The equipment used was a RVDV-II+P Viscometer utilizing the Rheocalc software. Due to the bio-crudes' physical conditions it was impossible to measure its viscosity at temperatures below 80°C and thus sent to the Mechanical Department of Aalborg University.

5.5.7 High Heating Value(HHV)

The purpose is to determine the Gross Calorific Value(Higher Heating Value HHV) of solid and liquid combustible materials.HHV is crucial as it measures the total energy content of a fuel, including the latent heat of vaporization of water. This comprehensive measure of energy efficiency is essential for evaluating the fuel's potential for energy production and its overall performance in combustion processes. HHV is particularly important in comparing different fuels, optimizing energy systems, and ensuring that fuels meet specific energy standards and environmental regulations. The equipment used is a Bomb Calorimeter IKA C2000 Basic, with oxygen supply quality 3.5 (99.95% pure). Though, for some experiments due to lack of sample HHV was calculated via the equation 5.6 proposed by Channiwala and Parikh. [38]

$$HHV(MJ/kg) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A$$

Figure 5.6: Equation for HHV calculation
[38]

5.5.8 Ash Content

The purpose of the procedure is to determine the ash content of the bio-crude examined. The equipment used was the Electric Muffle Furnace and the sample was inciterated at 775°C overnight. The ash content was measured by the mass of the remaining products afterwards.

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Chapter 6

Results and Discussion

6.1 Vacuum Distillation

A total of 897.33 g of bio-crude oil was placed in a flask with 208.66 g pure EtOH as a solvent. In the flask, a stirrer was placed at the bottom to ensure the proper mixing of the oil. Five distillation fractions were collected at different boiling points as the distillation temperature was increased. The first fraction was collected at <78°C. This fraction denoted a lower recovery since its main components are mainly the recovery from ethanol that was added. The second fraction was collected at 78°C until 150°C. Similarly, despite its high recovery, this fraction is mainly consisted of the recovery of ethanol added as well as some light fractions that got distilled. The third fraction was obtained at 150°C until 200°C. The recovery obtained in the container was the smallest compared to the others. The fourth fraction was collected at 200°C until 250°C. This one showed the highest recovery percentage of all. Finally, the last fraction was obtained at 250°C until 300°C. The products obtained are depicted in 6.1 and the yield distribution amongst the fractions are depicted in 6.1.

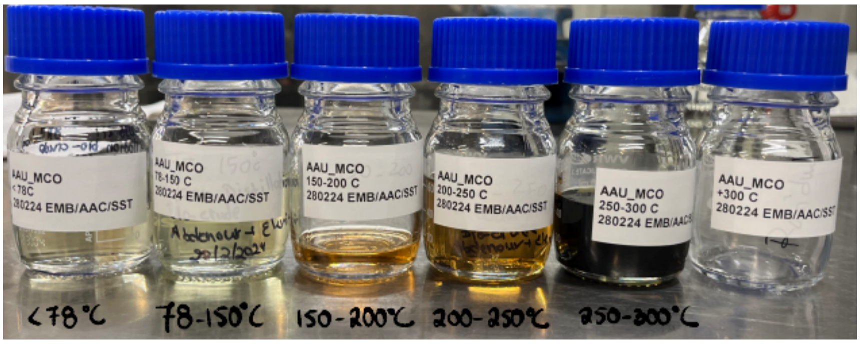


Figure 6.1: Distillation fractions obtained

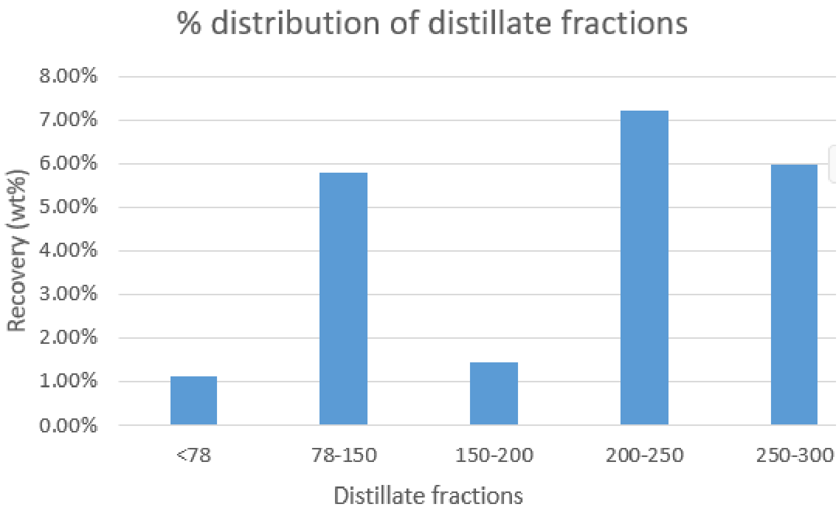


Figure 6.2: Yield distribution for distillation fractions

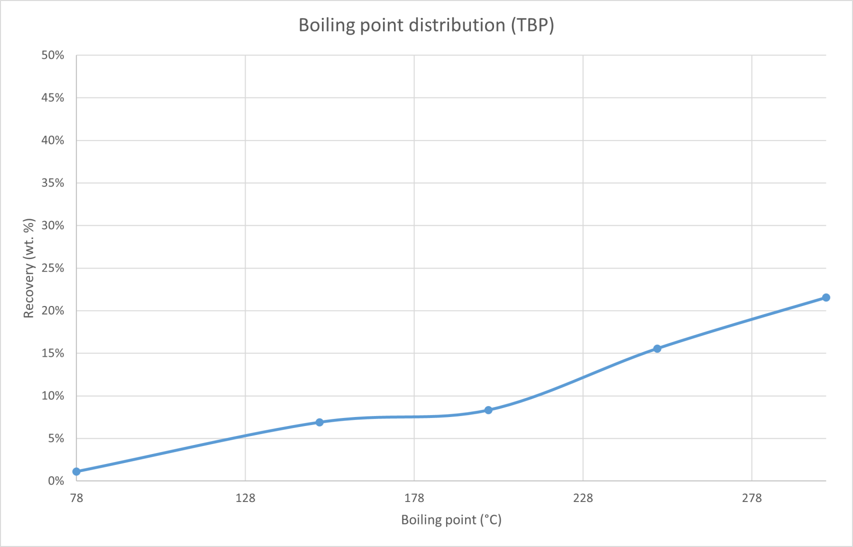


Figure 6.3: Boiling point distribution for distillation fractions

This boiling point distribution graph provides a comprehensive view of the distillation profile of biocrude. It reveals a steady increase in recovery across the temperature range, highlighting the presence of a mix of light to heavy hydrocarbons. Analytically, the initial low recovery at 78°C indicates minimal light fractions at the lower end of the temperature range. In the range of 78-150°C the recovery percentage increases slowly reaching approximately 5%. This gradual increase up to 178°C suggests the presence of lighter to mid-range hydrocarbons such as naphtha and kerosene. The recovery rises steadily as the temperature rises. The rate of recovery starts to accelerate between 178°]*textC* and 228°C. This range captures more significant fractions, with recovery rising to about 15%. From 228°C to 278°C, the recovery continues to increase, reaching up to 20%. This suggests that heavier fractions with higher boiling points are being collected likely including diesel and other heavier fractions. All things considered the overall product recovery was almost 21% with the rest being a bottom flask distillation residue. The residue was impossible to be collected since it could not be extracted and needed to be dissolved with Acetone, THF, DMSO, to be able to clean the flask. Thus, the analysis results would not be representative.

6.1.1 Elemental analysis of C,H,N,O

The elementary composition of the bio-crude distillation is depicted at the following table.

Fraction	Moisture Content	C	H	N	O	HHV
Below 78°C	3.63	34.33	9.03	0.00	60.40	25.67
78-150°C	6.48	35.51	9.14	0.31	61.97	25.80
150-200°C	1.25	61.97	9.26	0.53	29.50	29.03
200-250°C	1.15	69.66	8.90	0.82	21.78	34.73
250-300°C	0.48	67.79	8.29	0.98	23.41	33.35

Table 6.1: Elemental Composition of distillation fractions together with water content and HHV. All on wt% dry basis.

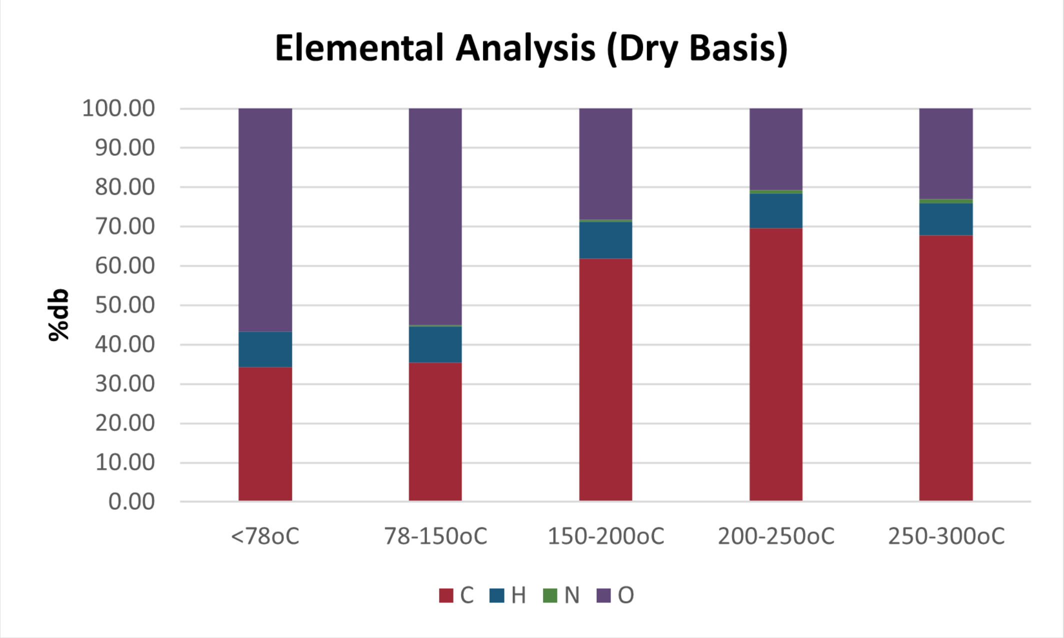


Figure 6.4: Elemental contribution of distillate fractions

The elements contributed at **??** demonstrate the deviation of C,H,N,O percentages in dry basis between the distillation fractions. As the boiling point range increases, the carbon content also increases. Heavier fractions tend to have more complex hydrocarbon structures, which contain higher amounts of carbon. The highest C concentration is observed at 200-250°C. On the other hand, the hydrogen content decreases with increasing boiling points. Lighter fractions are typically more hydrogenated, containing more simple and saturated hydrocarbons, whereas heavier fractions contain more aromatic and complex hydrocarbons with relatively lower hydrogen content. The highest H concentrated fraction appears to be the first one. Though, this fraction is mostly consisted of the solvent added EtOH and theoretically some very light elements. Nitrogen content is higher in the lighter fractions and decreases in the heavier fractions. Nitrogenous compounds often have lower boiling points and are more likely to be present in the lighter distillates. Finally, oxygen content is significantly higher in the lighter fractions and decreases with increasing boiling points. Oxygenated compounds, such as alcohols and acids, tend to have lower boiling points. As the distillation progresses, these are removed, leaving behind heavier, less oxygenated hydrocarbons.

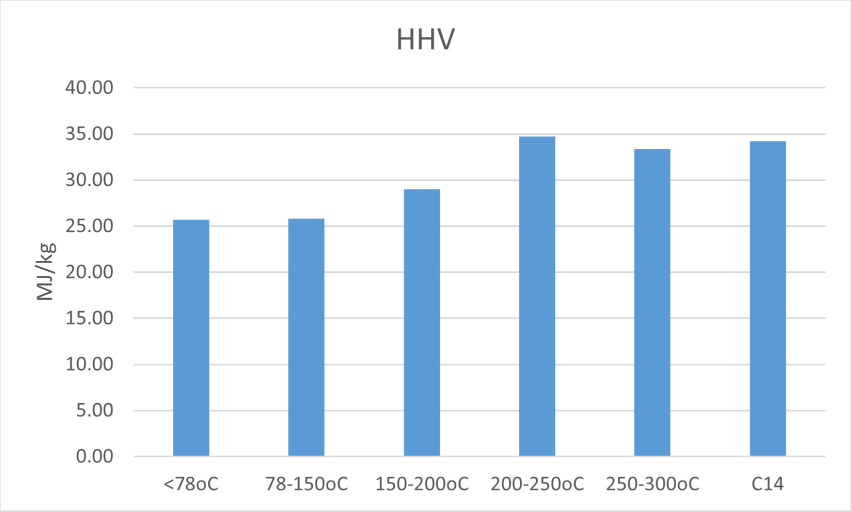


Figure 6.5: HHV of distillate fractions compared to C_14

6.5 presents the HHV (in MJ/kg) of different distillate fractions compared to the initial biocrude product C_14 after undergoing distillation. The fractions are categorized by their boiling point ranges. The initial biocrude has a high HHV, indicating that the distillation process effectively concentrates energy-dense components in specific fractions. The first fraction obtained (below 78°C) contains lighter hydrocarbons with a moderate energy content. It represents the more volatile components of the biocrude. From 78°C to 150°C the HHV increases. This increase indicates the presence of slightly heavier hydrocarbons, which typically have higher energy densities compared to the lightest fraction. As the boiling point increases, the hydrocarbons become more complex and energy-dense, resulting in a higher HHV. At 200-250°C it shows the highest HHV, indicating that it contains the most energy-dense hydrocarbons, making it highly suitable for fuel applications. Moreover, its value is slightly higher than the initial distillation product. While still high, the last fraction contains very heavy hydrocarbons, which might include components that slightly reduce the overall energy content compared to the 200-250°C fraction. Concluding, The HHV increases with higher boiling point fractions up to 200-250°C, indicating that mid-range fractions are the most energy-rich.

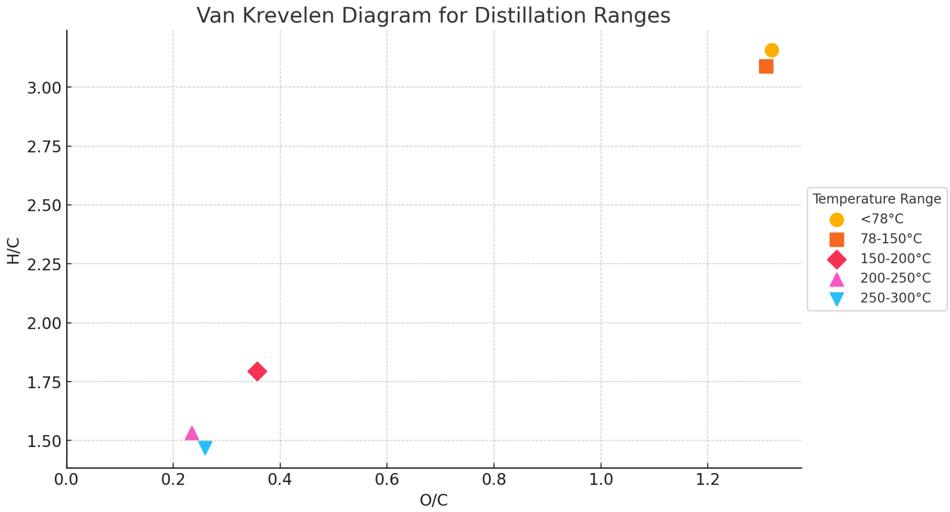


Figure 6.6: Van Kreevelen diagram for distillation fractions

Figure 6.6 satisfies the results obtained from the distillation fractions. The heavier fractions indicate a better H/C and O/C ratio whilst the lighter fractions are far away from the orego indicating a higher oxygenating ratio. The rate of decrease in both ratios was observed in fraction 200-250°C. This is a good indicator of blending with transportation fuels. Thus, this parameter will be discussed further in the report.

6.1.2 Simulated Distillation

Simulated distillation (Sim-Dis) analysis was performed to evaluate the boiling point distribution of the liquefied samples. Typical distillation cuts for transportation fuels are as follows: Gasoline (<190°C), jet fuel (190-290°C), diesel (290-340°C, vacuum gas oil (340-538°C), vacuum residue (above 538°C).

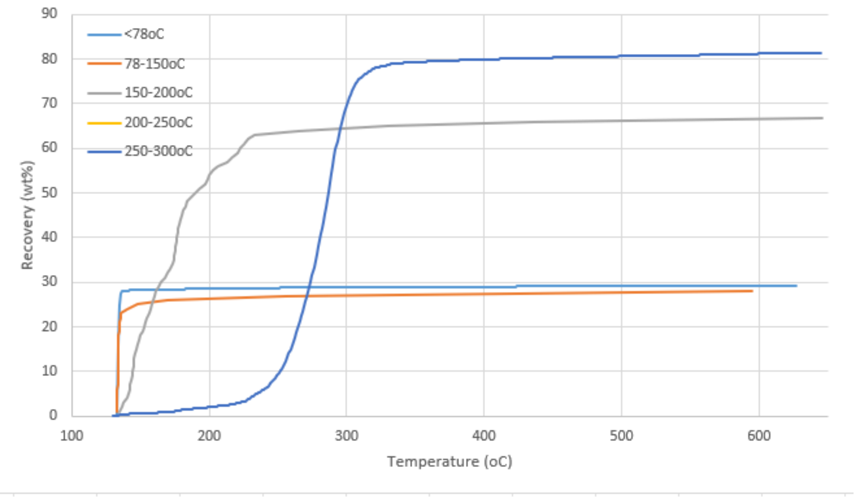


Figure 6.7: Simulated distillation curves of all distillation fractions

The investigation of the distillation curves reveals a desired trend of shifting to heavier fractions as expected. For the fraction below 78°C rapid recovery at lower temperatures indicates the presence of very light, highly volatile compounds. The recovery starts at around 100°C and quickly reaches 80% recovery by approximately 300°C, then plateaus. For the second fraction it starts recovering slightly later and increases steadily, reaching about 30% recovery. The curve remains relatively flat, indicating a slower increase in recovery, representing light hydrocarbons like naphtha. For 150-200°C it shows a significant increase starting around 150°C and reaches up to 70% recovery. This indicates the presence of middle distillates, including kerosene and light diesel. For 200-250°C the recovery begins at around 200°C, showing a steady rise to about 35% recovery. This fraction represents heavier hydrocarbons, suitable for diesel and other middle distillates. Lastly, the concluding fraction has the lowest recovery rates, starting at around 250°C and only reaching about 25% recovery. These are the heaviest fractions, indicating the presence of heavy oils and residuals.

Therefore, the contribution of the fuel fractions in respect to the distillation fractions after Sim-Dist is depicted at the table below:

Fraction	Gasoline	Jet Fuel	Diesel	VGO
Below 78°C	28.4	0.3	0.3	0.3
78-150°C	26	0	1	1
150-200°C	34	29	2	1.9
200-250°C	3	69.3	12.8	1.8
250-300°C	1	8.4	69.8	2.2

Table 6.2: Contribution of the fuel fractions after Sim-Dist in respect to the distillation fractions.Measured in wt%

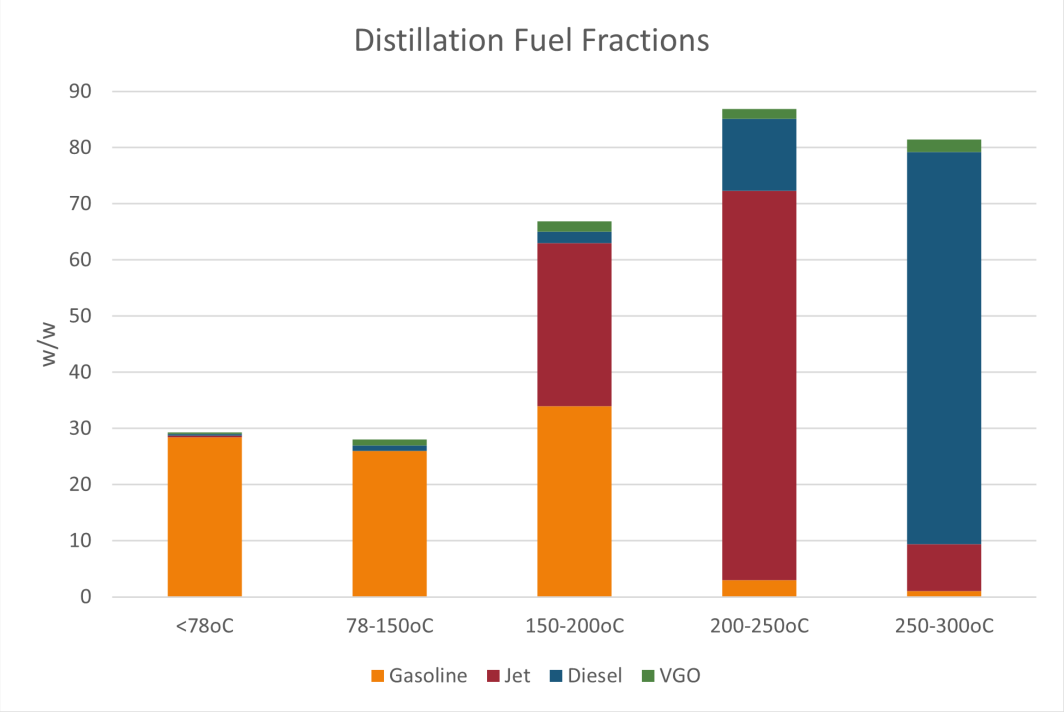


Figure 6.8: Virtual Contribution of the fuel fractions after Sim-Dist regarding the distillation fractions. Calculated in wt%.

The chart clearly demonstrates the expected trend where lighter fractions like gasoline dominate at lower temperatures, while heavier fractions like diesel and VGO appear at higher temperatures. It is observed that in lower distillation fractions (<78°C) , (78-150°C) the contribution of fuel fractions is less in comparison to the higher ones. The gasoline fraction is predominantly present in the lower temperature ranges, aligning with its characteristic of boiling off early in the distillation process. Its presence diminishes significantly in the higher temperature ranges. As the °C increases jet fuel becomes significant in the 150-200°C range and is the major component in the 200-250°C range. This trend is consistent with the typical boiling point range of jet fuel. For the last fraction (250-300°C) the diesel fraction contribution increases significantly compared to the other fractions. Lastly, VGO has a minor presence across all temperature ranges but shows a noticeable increase in the last distillation fraction as expected.

6.1.3 Viscosity

Viscosity is a critical parameter in the evaluation of fuel performance, as it affects the fluid's flow characteristics and its ability to atomize during combustion. The study of viscosity across varying shear rates helps understand the rheological behavior of bio-crude, providing insights into its stability and suitability for use in engines. By analyzing how viscosity changes with shear rate, we can determine the non-Newtonian properties of the fluid, which are essential for optimizing the fuel refining process and ensuring consistent performance in practical applications. The viscosity test was executed at the Mechanical Department of Aalborg University.

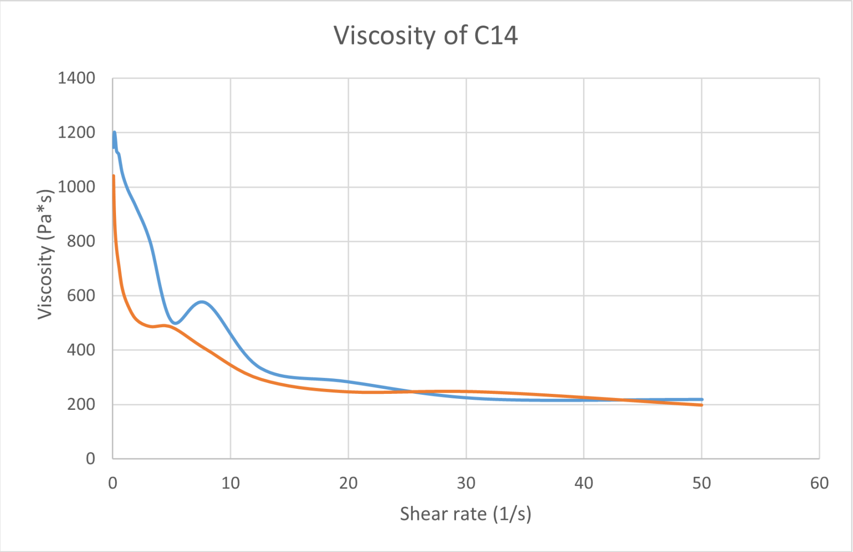


Figure 6.9: Viscosity of C_14

The provided chart illustrates the relationship between shear rate (1/s) and viscosity (Pa.s) for two trials of the biocrude sample of C_14. The viscosity is exceedingly high, topping 1000 Pa.s in both trials at very low shear rates (<1/s). This suggests that, like many complex organic liquids, the biocrude is extremely viscous when subjected to small shear.The viscosity decreases sharply as the shear rate rises from 0 to about 5 1/s. This behavior points to shear-thinning characteristics, in which the fluid's viscosity decreases with increasing shear rate. Non-Newtonian fluids frequently have this property, especially ones with intricate molecular structures like biocrude. The viscosity levels off and gradually drops at a considerably slower pace after a shear rate of about 10 1/s. The viscosity stabilizes at about 200 Pa.s at higher shear rates (20-50 1/s), suggesting that the fluid achieves a more uniform flow behavior at high shear settings. With just little differences in viscosity values at matching shear rates, both trials exhibit comparable trends. The resilience of the rheological characteristics of the biocrude sample is indicated by this consistency, which implies dependable reproducibility of the experiments. The significant reduction in viscosity with increasing shear rate implies that the biocrude will flow more easily under high shear conditions, such as those found in fuel injection systems. This is beneficial for efficient fuel atomization and combustion.

6.1.4 TAN

Total Acid Number (TAN) is a crucial parameter in evaluating the acidity of fuels, including biocrude. It quantifies the amount of acidic components in a fuel sample, measured in milligrams of potassium hydroxide (mg KOH) required to neutralize one gram of the sample. High TAN values indicate higher acidity, which can lead to corrosion of storage and engine components, affecting fuel stability and performance.

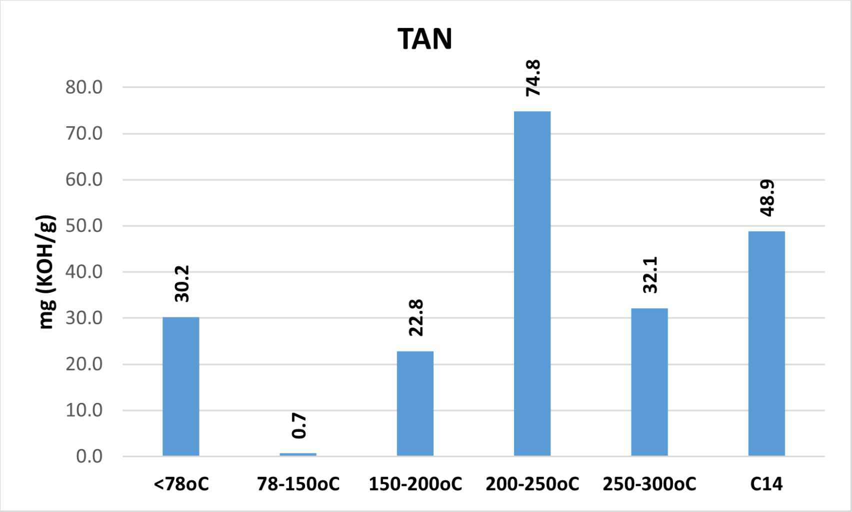


Figure 6.10: TAN number of distilled fractions in regard to C_14

6.10 displays the TAN values (in mg KOH/g) for various distillation fractions compared to the initial biocrude C_14. The initial biocrude (C_14) shows high acidity, typical of raw biocrude containing various acidic components. The TAN values indicate that the acidity is not uniformly distributed across the fractions. Fraction < 78°C shows significant acidity, indicating a high presence of light, acidic compounds. Continuing on, at fraction 78-150°C the acidity is minimal in this fraction, suggesting effective separation of acidic components in lighter fractions. Fraction

150-200°C shows moderate level of acidity which might include mid-weight acidic compounds. The highest acidity level is observed at fraction 200- 250°C. This could be an indicator of not proper-breakdown of the lignocellulosic compounds. Also, after liquefaction there is an often formation of small carboxylic acids such as formic and acetic acids. Thus, GC-MS analysis could proper characterize the compounds and justify the results. In the last distilled fraction the acidity level is still high but it shows a reduce.

6.1.5 Conclusion

In this chapter, we conducted a detailed distillation of biocrude oil mixed with ethanol to analyze various distillate fractions. The process yielded five distinct fractions, each characterized by its boiling point range and unique properties. The distribution graph of boiling points demonstrated the effective separation of hydrocarbons by confirming a consistent rise in recovery. With increased boiling temperatures, elemental analysis revealed a drop in hydrogen, nitrogen, and oxygen concentration and an increase in carbon content. This pattern is consistent with heavier hydrocarbons' chemical makeup. At 200–250°C, the greatest energy-dense percentage was detected by HHV, suggesting that it could find use as fuel. While the TAN study found varied amounts of acidity across fractions, with the maximum acidity in the 200–250°C range, requiring further treatment for stability, the viscosity analysis demonstrated shear-thinning behavior, which is advantageous for fuel injection systems.

6.2 Filtration of initial cycles

The next step of the experimental work was to filtrate C_7, C_9, C_11, C_14 of the bio-crude with THF and Tol/IPA. The ratios accumulated were (1:5) and (1:4:1) respectively, as suggested by Simon Ruwe [39] after a trial of different ratios and solvents. Thus, this information is unrelated to this project, and therefore will not be explained in further detail. [39]. In the next figure, the oil yield and solid removal are represented.

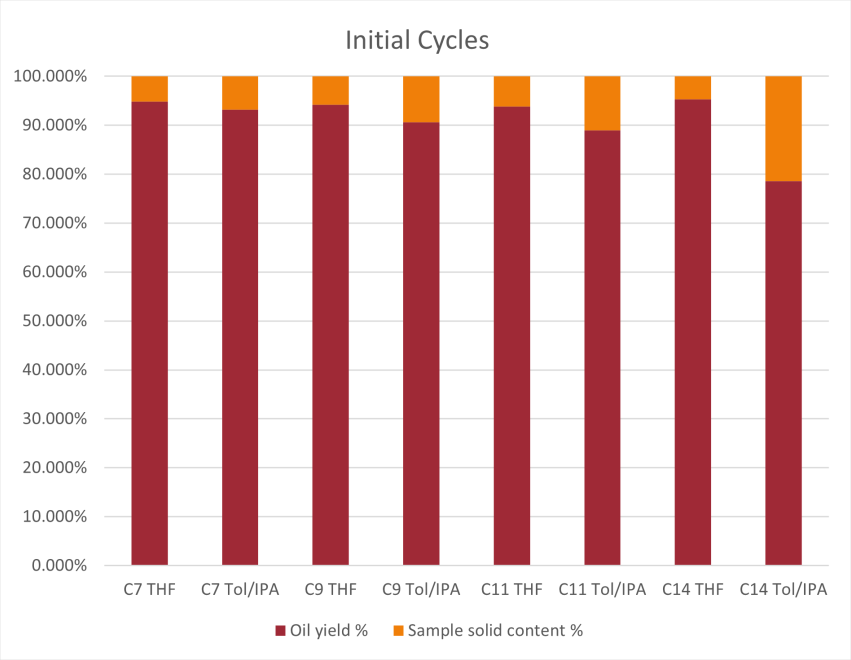


Figure 6.11: Oil Solid yields of C_7, C_9, C_11, C_14. Measured in wt%

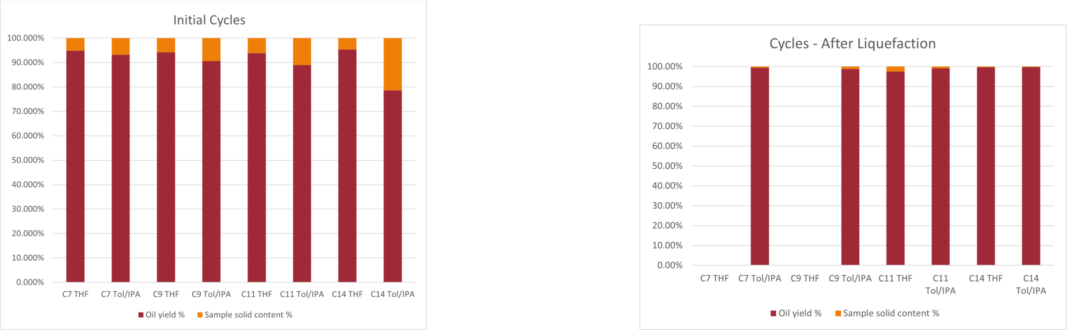
Across all cycles and solvents, the oil yield remains consistently high, close to 90-95%. This indicates efficient extraction and separation processes, ensuring maximum recovery of biocrude. The solid content is relatively low in all cases, around 5-10%, indicating effective removal of solids during the separation process. There is a slight variation in solid content between THF and Tol/IPA, with Tol/IPA showing marginally lower solid content in some cycles and especially C_7. However, While the cycles increase so does the solid content as well. The highest solid/ oil separation is observed in C_{14} specifically with the Tol/IPA mixture. This chart will be subsequent for comparison with the solids after liquefaction experiments. No further analysis were investigated at this part of the experimental work since it is not the main objective.

6.3 Experimental Analysis for liquefaction

The experimental setup for the liquefaction process in the micro-batch reactor was explained in Table 4.1. The process stood a great need of added EtOH as a solvent for recycling since the physical properties would not allow proper mixing during the procedure.. In total 10% of the initial weight was added to each sample. The operating conditions of each experiment were executed at 350°C constant for 15 min with 60 bar Nitrogen added.

6.3.1 Solids removal after liquefaction

With the termination of the process, all the experimental products were collected with the respective solvent mixture that was used for their filtration and filtrated again. This is crucial, being that during liquefaction in high temperature a formation of solids is possible. Therefore, the results before liquefaction and after liquefaction in terms of oil yield and sample solid content were calculated and depicted below.



(a) Oil and solid yields of initial cycles

(b) Oil and solid yields after liquefaction

Figure 6.12: Oil and Solid yields a)before and b)after liquefaction. All calculated at wt%

For experiments C_7+THF+10% EtOH and C_9+THF+10% EtOH solids were not calculated and due to a limitation of the original sample were not repeated after. It is observed that the production of solids after liquefaction was minimal except for C_{11} which shows the maximum production compared to other cycles.This is an important parameter, since the solids will alter further analysis and also will affect the bio-crude in further treatment. Compared to the filtration of the initial cycles the same trends are being followed for $C_1$1, whilst the production of solids for the rest of the cycles is minimized.

6.3.2 Elemental analysis C,H,N,O

The elementary composition after the liquefaction experiments is depicted at the following table.

Experiment	Water content	C	H	N	O	HHV
C_7+THF+10%EtOH	1.124	80.35	9.36	1.03	10.39	37.42
C_7+Tol/IPA+10%EtOH	3.623	82.17	9.20	0.93	11.47	37.75
C_9+THF+10%EtOH	3.402	80.75	9.09	0.98	12.70	37.01
C_9+Tol/IPA+10%EtOH	2.515	82.01	9.21	0.54	10.81	37.78
$C_1$1+THF+10%EtOH	4.072	81.65	8.78	0.23	13.58	36.86
$C_1$1+Tol/IPA+10%EtOH	4.091	81.36	8.86	1.00	13.05	36.91
$C_1$4+THF+10%EtOH	-	75.97	7.79	0.23	16.02	33.49
$C_1$4+Tol/IPA+10%EtOH	6.419	84.30	8.57	0.94	12.46	37.64

Table 6.3: Elemental Composition of experiments after liquefaction together with water content, HHV.All on wt% dry basis

All the results are obtained in wt%. Though, for $C_1$4+THF+10% EtOH it was impossible to measure the H_2O content since the sample was in a solid form after the removal of the solvent, making it impossible to extract it. O was calculated by a substraction.

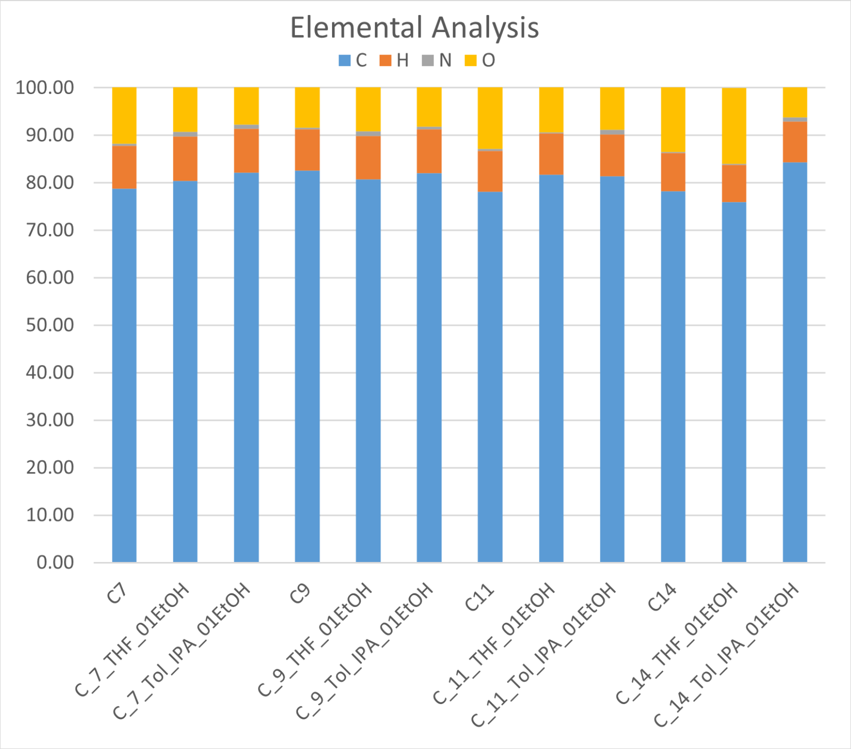


Figure 6.13: Elementary analysis in products after liquefaction in comparison to its respective initial cycle.Measured in dry basis

Across all cycles and solvent treatments, carbon content remains consistently high, around 75-80%. The highest carbon content is depicted at the last experiment. Hydrogen content is relatively stable, ranging from 8-10% with the highest content on C_14+THF+10% EtOH. Nitrogen content is low, around 0-2%, across all samples. Lower nitrogen content is beneficial as it reduces NO_x emissions during combustion. Oxygen content varies significantly, typically between 10-15%. All in all, carbon and hydrogen content remain consistent across different cycles, suggesting that the liquefaction process and solid removal are effective in maintaining the quality of biocrude. Oxygen content shows some variability, which could be due to differences in solvent interactions during the solid removal process. Solvent mixtures may influence the removal of oxygenated compounds, as seen in varying oxygen content. Tol/IPA treatment appears to enhance the removal of oxygen and nitrogen compounds, leading to higher carbon and slightly lower hydrogen content. This suggests that this solvent is effective in concentrating the carbon content and improving the overall quality of the bio-crude.The initial cycles show higher variability in elemental composition, reflecting the raw biocrude's diverse mixture. The carbon content is slightly lower, and the oxygen content is higher compared to solvent-treated samples, indicating the raw biocrude's complexity and presence of more oxygenated compounds.

In comparison with the initial cycles, there is a slight but not remarkable improvement in the content of carbon efficiency and oxygen reduction especially for C_14. Though, the state of the product combined with the analysis indicate that it need further upgrading.

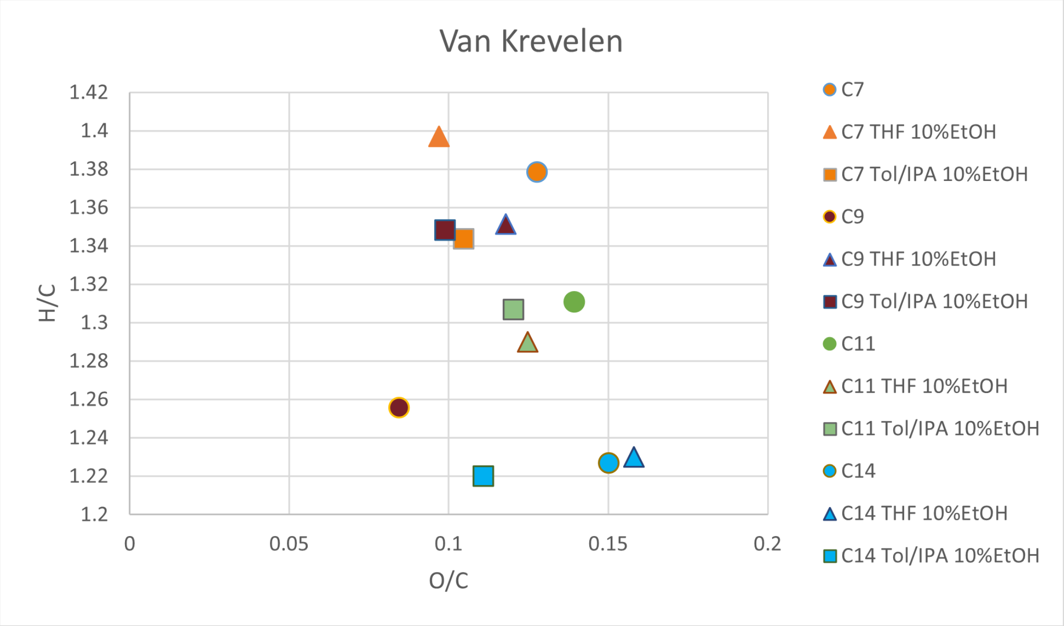


Figure 6.14: Van Kreevelen diagram after liquefaction

Figure 6.14 ensures the obtained results from the elementary analysis and depicts the variance between the different experimental setups. All in all,the data suggest that Tol/IPA mixtures are particularly effective in deoxygenation. Though,all of the samples are quiet far from the H/C axis indicating that it cannot be blended with maritime fuel and needs further upgrading. The most closer to the blending scenario could be C_7 with both solvent treatment methods.

6.3.3 HHV

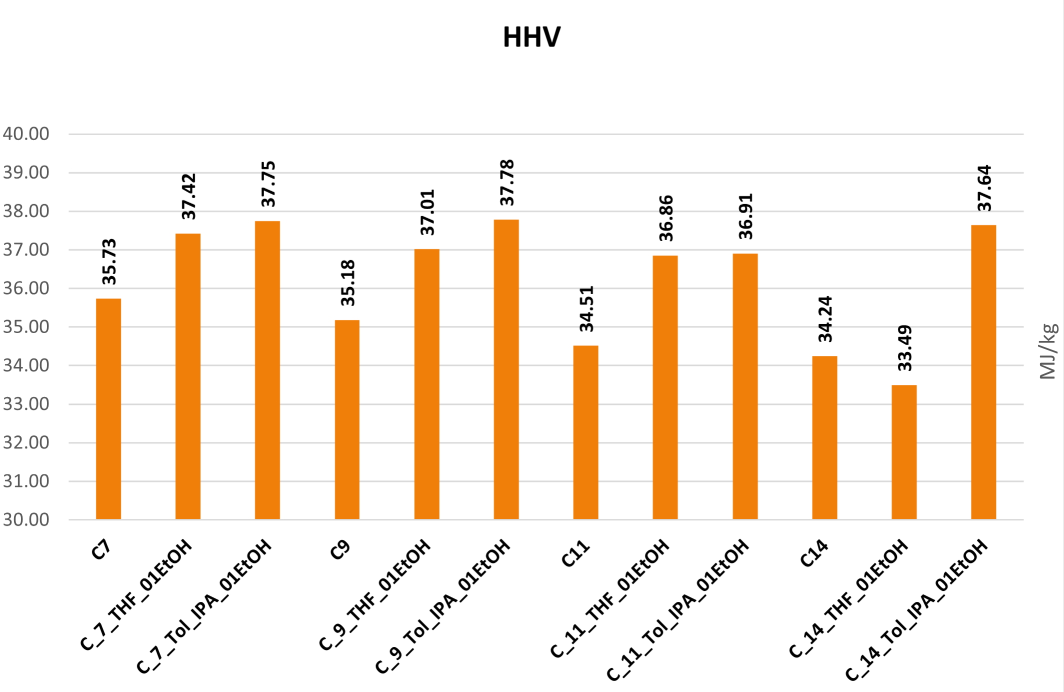


Figure 6.15: HHV after liquefaction in respect to initial cycles

HHV was calculated through the empirical formula of 5.6 since the samples after the experiments were not sufficient in amount.

6.15 depicts the HHV (in MJ/kg) for various experimental samples compared to the initial cycles after solid separation by THF and a mixture of Tol/IPA.

The initial cycles show constant HHV readings, indicating that the untreated bio crude's energy content is steady. In comparison to the first cycles, the solvent-treated samples typically exhibit higher HHV, indicating higher energy content. The samples C_9 and C_{14} that were treated with Tol/IPA had the highest HHV. The greater HHV values in these samples suggest that the use of solvents appears to increase the energy content of the biocrude. This implies that energy-dense hydrocarbons can be concentrated with the aid of these solvents. The highest

HHV values are obtained from the solvent treatments of Tol/IPA, especially in the C_9 and C_{14} cycles. This suggests that these solvents are more successful in raising the biocrude's energy content.

HHV is connected directly with the energy recovery. Thus, the energy recovery was calculated for the bio-crude after liquefaction. The formula used is displayed below:

$$\text{Energy Recovery (\%)} = \left(\frac{\text{HHV of biocrude}}{\text{HHV of feedstock}}\right) \times \text{biocrude yield} \tag{6.1}$$

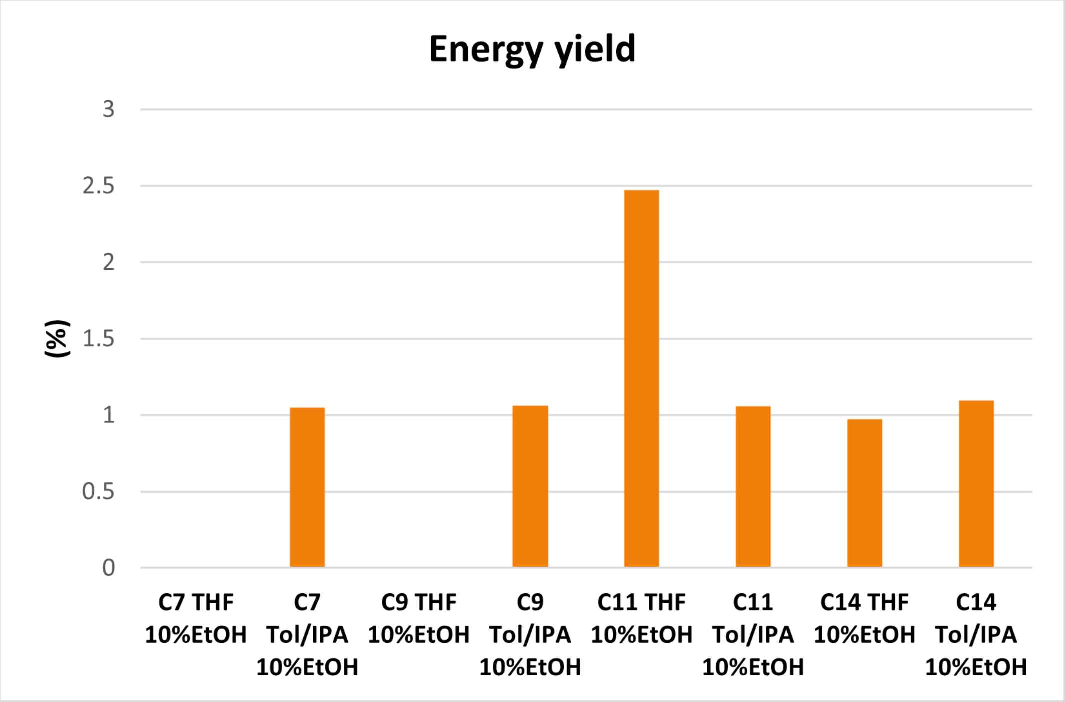


Figure 6.16: Energy Recovery of experiments

6.16 depicts the energy recovery from all the experiments executed after liquefaction. For experiments of C_7 and C_9 with THF the oil yield was not calculated. From the chart, it is evident that the energy recovery varies across different solvents and cycle combinations. Notably, the C_{11} THF 10combination achieves the highest energy recovery at approximately 2.5%. This indicates a significant improvement in energy recovery for this specific combination and cycle, suggesting that THF with 10% EtOH is highly effective at this cycle. Conversely, other combinations such as C_7 THF 10%EtOH and C_9 Tol/IPA 10%EtOH show lower energy recoveries, around 1% or less, indicating less efficiency in those conditions. These results show contrary results to HHV, which for instance, in the case of C_9 Tol/IPA show a higher HHV in contrast to C_{11} THF.

6.3.4 Simulated Distillation (SimDist)

The provided SimDis results show the recovery percentage (wt%) of various experimental samples after liquefaction, plotted against temperature ∘C. The experiments include different cycles treated with solvents such as THF, Tol/IPA and Ethanol as an added solvent(10%).

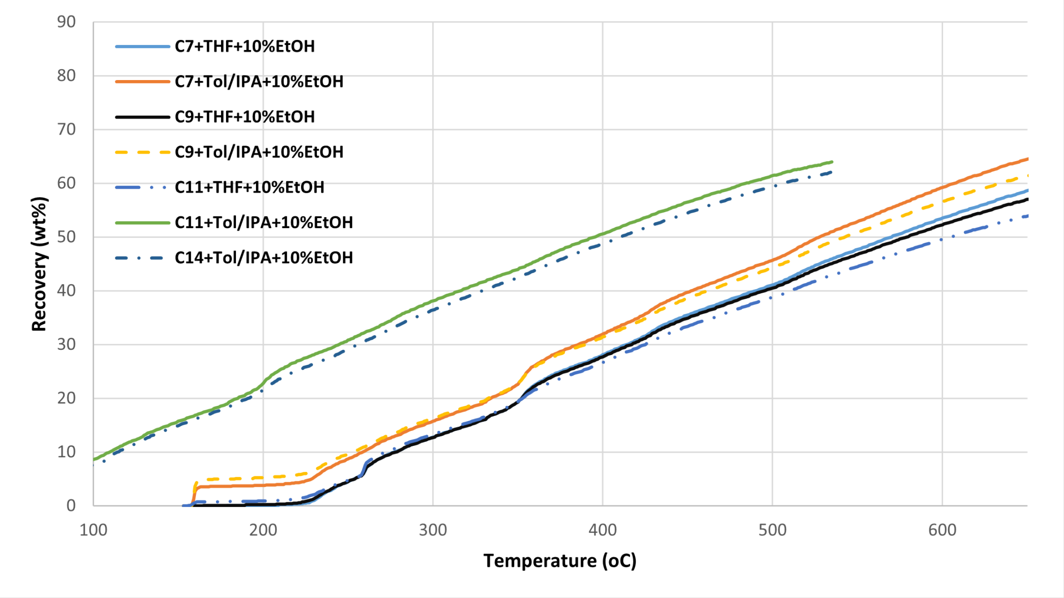


Figure 6.17: SimDist results after liquefaction

All samples exhibit minimal recovery at low temperatures (below 200°C), indicating the presence of very light, volatile compounds. The recovery starts to increase more significantly beyond this temperature range. C_7 and C_9 with THF show a gradual increase in recovery, reaching around 50-60% at 400°C. The steady rise indicates the presence of middle distillates, such as kerosene and light diesel. Similar behavior is observed with these samples treated with Tol/IPA, but the recovery is slightly higher, indicating a more significant presence of middle distillates. The recovery continues to increase steadily beyond 400°C for $C_1$1 and $C_1$4, reaching up to 80-85% at 600°C. These fractions represent heavier hydrocarbons. The samples treated with Tol/IPA show slightly higher recovery rates, suggesting better efficiency in extracting heavier fractions. The recovery trends are consistent across different cycles with slight variations in recovery percentages. This consistency suggests reliable reproducibility of the liquefaction process and solvent treatment effects.

Therefore, the contribution of the fuel fractions in respect to different experiments is depicted at the table below:

Experiment	Gasoline	Jet fuel	Diesel	VGO
C7+THF+10%EtOH	0	4.5	13.4	43.8
C7+Tol/IPA+10%EtOH	3.5	5.1	12.5	46.3
C9+THF+10%EtOH	0.1	4.4	13.4	41.6
C9+Tol/IPA+10%EtOH	5	4.6	11.8	42.6
C11+THF+10%EtOH	0.7	4	13.5	38.1
C11+Tol/IPA+10%EtOH	4	4.4	12.5	43.1
C14+THF+10%EtOH	3.7	3.8	12.6	42

Table 6.4: Contribution of fuel fractions after Sim-Dist for different experiments

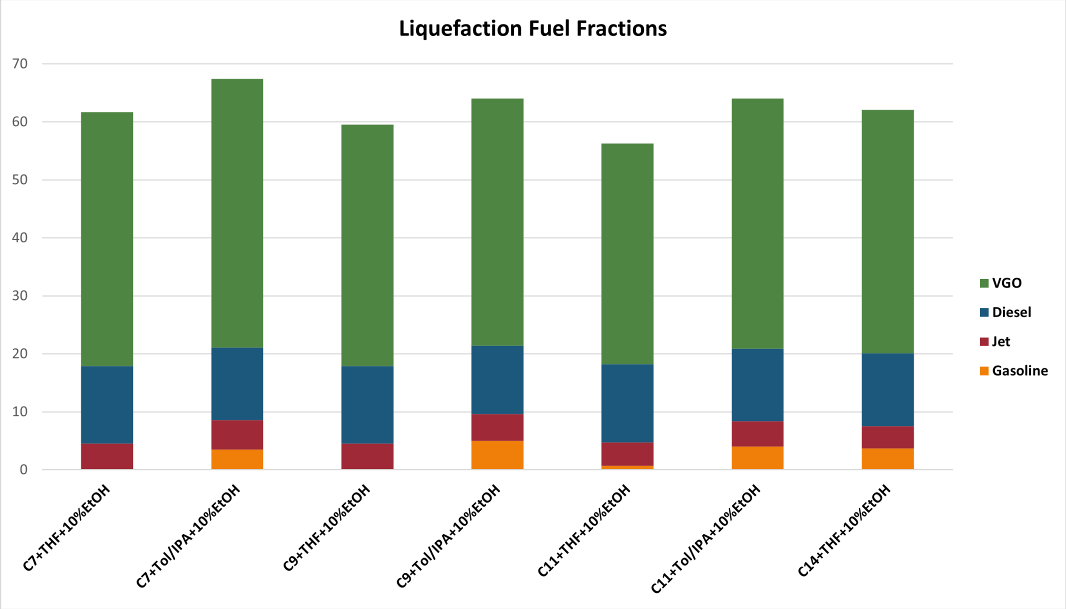


Figure 6.18: Virtual Contribution of the fuel fractions of different experiments after liquefaction

With VGO consistently above 50% of the fuel fractions in all solvent and cycle combinations, heavy oil accounts for a sizable component of the liquefaction result. With an average distribution between 20% and 30%, diesel is the second most abundant fraction among all combinations, demonstrating the process's efficiency in creating fuels with intermediate boiling points. Although it is continuously present in all combinations, jet fuel exhibits a lesser fraction of 10% to 15%, indicating that some portion of the product is within the boiling range of jet fuel. Compared to heavier fractions, gasoline is the least plentiful fraction and contributes the least percentage, usually less than 10%. This suggests that less light ends are produced throughout the liquefaction process.

Comparing THF with Toluene/IPA, both solvent mixtures show similar trends in fuel fraction distribution, with slight variations such as a marginally higher Diesel percentage with Toluene/IPA in some cycles, but overall, the solvent choice does not drastically change the product distribution. The fuel fraction distribution is mostly unaffected in different cycles, with all cycles showing a similar trend where VGO is the predominant percentage followed by Diesel, Jet, and Gasoline. The liquefaction technique is particularly effective in creating heavy oil fractions, as seen by the consistently high VGO concentration across all combinations. The comparatively constant distribution of gasoline, diesel, and jet across a range of solvents and cycles points to a reliable procedure that is not overly dependent on these factors.

It is also observed that the fractions are not fully measured. This could be an indicator of improper equipment calibration,losses or improper sample dissolvement in CS_2 solvent that was used for this analysis.

6.3.5 TAN

The provided table and chart illustrates the Total Acid Number (TAN) values (mg KOH/g) for various experimental samples after liquefaction, compared to the initial cycles treated with different solvents and with EtOH solvent added during the liquefaction process. C_{14} treated with THF and 10% EtOH could not be measured since the sample was in solid form and therefore could not be extracted.

Experiment	TAN
C7	32.5
C7 + THF + EtOH	15.8
C7 + Tol/IPA + EtOH	16.4
C7 + Tol/IPA + EtOH	18.7
C9	33.5
C9 + THF + EtOH	18.7
C9 + Tol/IPA + EtOH	16.9
C11	28.6
C11 + THF +EtOH	17.6
C11 + Tol/IPA + EtOH	15.5
C14	30.2
C14 + THF + EtOH	0.0
C14 + Tol/IPA + EtOH	17.2

Table 6.5: TAN number after liquefaction

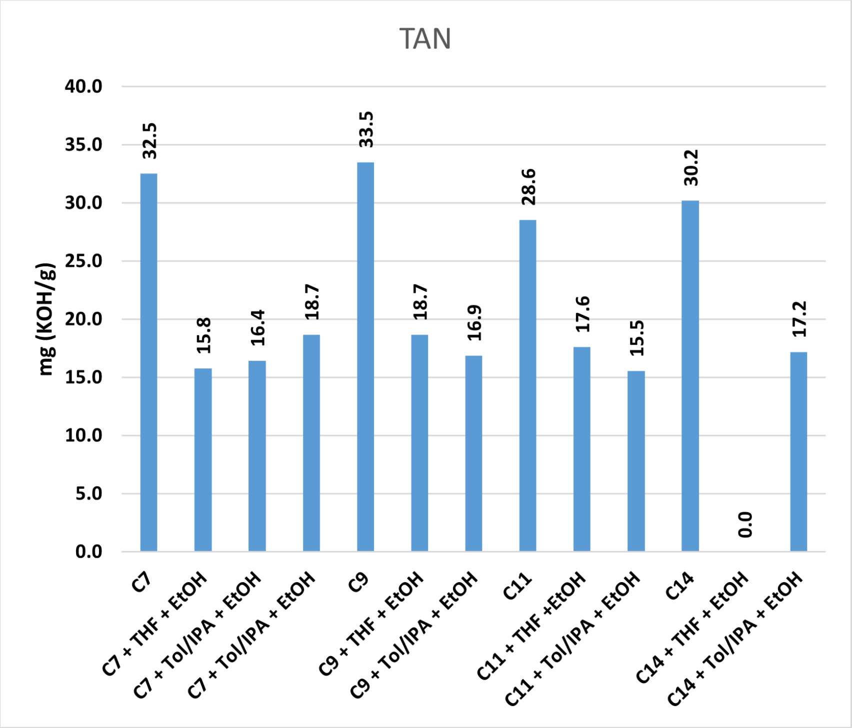


Figure 6.19: TAN after liquefaction in regard to its respected cycles

The initial cycles display relatively high TAN values, indicating significant acidic content in the raw biocrude. As we move in further cycles there is a drop in the acidic number. The solvents effectively lower the TAN values, particularly Tol/IPA, which show the most significant reduction in acidity. This suggests these solvents are more efficient in neutralizing acidic components. Though, the variation between all the experiments is significant low indicating that not much is changed or at least improved rapidly.

6.3.6 GC-Gas

Gas Chromatography (GC) is a powerful analytical technique used to separate and analyze compounds that can be vaporized without decomposition. The peaks were based in existing calibration data provided.

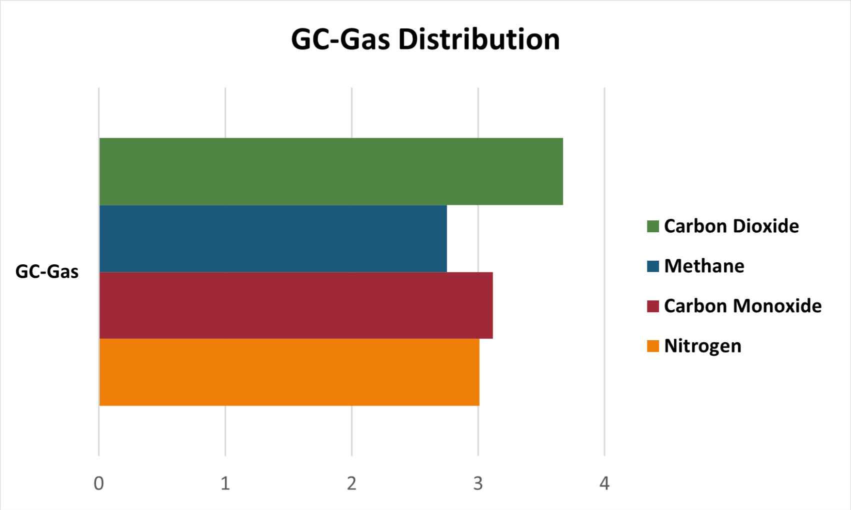


Figure 6.20: GC-Gas after liquefaction

6.20 chart shows the mean values of different gases (Nitrogen, Carbon Monoxide, Methane, and Carbon Dioxide) produced during the liquefaction process. There is around 3% of nitrogen in the mixture. Usually, nitrogen comes from two sources: the air and nitrogenous molecules found in biomass. Its presence is anticipated and shows how organic molecules containing nitrogen are breaking down throughout the liquefaction process.An observation of 3.2% CO by volume is made. One frequent byproduct of thermal breakdown processes, such as liquefaction, is carbon monoxide. It develops as a result of carbonaceous compounds partially oxidizing. The presence of CO indicates that the biomass feedstock was not fully burned or pyrolyzed. Methane makes up about 3% of the total volume. Its existence suggests that light hydrocarbons are produced during the liquefaction process. The most prevalent gas is CO_2, which has a concentration of roughly 3.5% by volume. The full oxidation of the carbon in the biomass fuel produces carbon dioxide. Significant oxidative breakdown is indicated by its high content, which is to be expected in a high-temperature liquefaction process. In summary, the amount of oxidation reactions taking place during liquefaction is indicated by the presence of CO and CO_2. While the presence of CO suggests locations where oxidation may be partial, higher CO_2 levels indicate effective oxidative breakdown. The development of valuable light hydrocarbons, which can be used as an extra energy source, is highlighted by the generation of CH_4.

6.3.7 Conclusion

Using a micro-batch reactor system, the experimental investigation examined the effects of several solvent treatments on the liquefaction of biocrude oil. The following are some of the chapter's major conclusions. With the exception of C11, which had higher solid yields, most trials successfully eliminated the solid content after liquefaction. For the bio-oil to become more stable and of higher quality, solids must be removed. All samples had a constant high carbon content (75–80%), with later cycles and those that had been solvent-treated showing the highest levels. The oxygen level ranged from 10 to 15%, and the Tol/IPA treatments demonstrated efficient deoxygenation, leading to increased carbon content and enhanced quality of bio-crude. In general, the solvent-treated samples' HHV was higher than it was in the first cycles. This suggests that energy-dense hydrocarbons are concentrated during solvent treatments, increasing the energy content of the biocrude. At temperatures below 200°C, recovery profiles showed little recovery; at temperatures above this range, recovery increased significantly. Samples treated with Tol/IPA showed improved recovery rates, particularly for middle and heavy distillates, indicating effective hydrocarbon extraction. TAN levels were successfully lowered by solvent treatments; Tol/IPA demonstrated the greatest reduction. This suggests that these solvents are effective at neutralizing acidic substances, enhancing the stability of the fuel.

6.4 Possibility of blending with crude-oil

Blending biocrude with petroleum-based crude oils represents a promising approach to enhancing the utilization of renewable energy sources within existing fossil fuel infrastructure. The goal of this technique is to create drop-in fuels that satisfies the strict requirements for transportation fuels by utilizing the complementing qualities of both fuel types. Analyzing the elemental composition of biocrude is necessary to determine whether it is compatible with blending. One useful tool for this analysis is the Van Krevelen diagram, which contrasts the ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) in biocrude with those of regular petroleum crude. In the end, this comparison contributes to a more sustainable energy future by pointing out the refinement steps that must be taken to optimize the mix for performance, stability, and environmental compliance. Since the experiments conducted are not upgraded it is irrational to compare with already upgraded maritime fuel. Therefore, the composition of petroleum crude-oil was quoted by [40] and depicted on the table below. The minimum and maximum value were obtained to create the diagram.

C	83% to 87%
H	10% to 14%
N	0.1 to 2%
O	O.05% to 1.5%

Table 6.6: Petroleum Crude Oil chemical composition

Two values, the highest denoted as P.B.(H) and the lowest denoted as P.B.(L) were obtained to form the Van Krevelen diagram illustrated below.

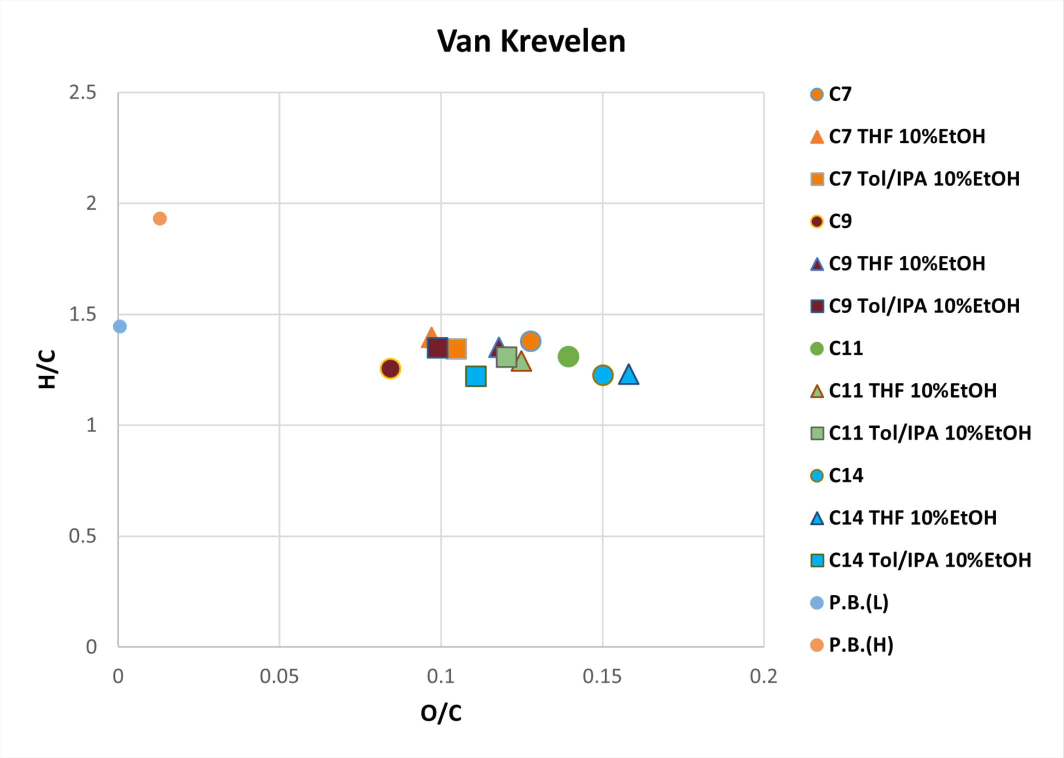


Figure 6.21: Van Krevelen between the petroleum crude-oil and experimental results after liquefaction

Observations reveal that most experimental points cluster within an O/C ratio range of 0.05 to 0.15 and an H/C ratio between 1 and 1.5. This clustering suggests a similar elemental composition across these samples, indicating a consistent process outcome. Notably, the point representing C_7 THF 10%EtOH stands out with a higher H/C ratio nearing 2, suggesting a higher hydrogen content compared to other samples. The reference points for petroleum crude oil exhibit lower O/C ratios and a broader range of H/C ratios, underscoring distinct chemical characteristics compared to the experimental samples. It is also observed that as we move further to cycles the points move further from the orego. Thus, the blending for these experiments with a petroleum crude-oil is not optional or preferred. Though, C_7 shows potential for further blending after further upgrading.

Chapter 7

Conclusion

The investigation conducted in this thesis on the co-processing of bio-crude distillate into the liquefaction process for drop-in biofuel production has yielded significant insights about how this technique can be integrated into current refinery processes and used to improve the quality of biofuel. We investigated the effects of different solvent treatments and cycles on the composition, HHV,TAN, GC-MS,Sim-Dist and general quality of bio-crude through a series of meticulously planned experiments, offering a thorough grasp of its transformation and possible applications.

Some of the key findings of this project were observed throughout the physical and chemical properties after liquefaction. In detail, after liquefaction, the elemental analysis showed that all cycles had a high carbon content that was consistently between 75 and 80%, with differences in the contents of Hydrogen, Nitrogen, and Oxygen based on the solvent treatment applied. The reduction of oxygen and nitrogen content, which improved the carbon concentration and general quality of the bio-crude, was made possible mostly by the Tol/IPA solvent mixture. Following solvent treatment, the HHV of the bio-crude samples improved, especially with the Tol/IPA mixture, which had the greatest energy content of all the studied samples. This improvement shows how much energy-dense hydrocarbons are present in the bio-crude, which makes it a more effective fuel source. As a result of increased recovery rates at higher temperatures and a more advantageous distribution of middle and heavy distillates appropriate for use as transportation fuels, the results of the study indicated that the samples treated with solvents had an advantage over the initial bio-crude produced. The biocrude's acidity, as measured by the TAN values, significantly decreased following solvent treatment, particularly when Tol/IPA was used. Reduced acidity improves the stability and performance of the gasoline by lowering the chance of corrosion in storage and engine components. Following liquefaction, the GC-Gas analysis revealed the presence of gases such as $C0_2$, CO, CH_4. Evaluating the liquefaction process's efficiency and influence on the environment requires an understanding of the composition of these gases.

Though, the viscosity after its samples separation of solids and liquefaction was not improved by sight. Unfortunately, this analysis measurement was not viable due to very small amount of product sample.

The investigation also delved into the possibility of mixing with currently available petroleum fuels. It became clear from comparing the van Krevelen diagrams of petroleum and bio-crude that, despite tremendous advancements, more upgrading is necessary to render bio-crude completely compatible with petroleum refineries. The van Krevelen diagram shows that the bio-crude has the potential to be blended because it is close to the H/C and O/C axes, but it also emphasizes the necessity of additional hydrogenation and deoxygenation processes.

With all being said, the author would like to conclude that the solid removal in earlier cycles would overall be beneficial for further processing. Though, an unexpected indicator of high solid production was observed in C_{14}. Moreover, the chemical composition was improved throughout the different experiments as well as continuing further to the cycles. However, this improvement was not as substantial indicating further upgrading as mentioned earlier. Lastly, the physical properties of the bio-crude after liquefaction of each cycle were not tremendously improved by sight but no further analysis has been conducted due to sample limitation.

Chapter 8

Future work

In the pursuit of advancing bio-crude production, the findings of this study suggest several areas for future research.

First of all, in regard to solid removal more research into various solvent combinations and their ratios may produce even more improved bio-crude quality. It would also be beneficial to extract the solids in the first few cycles before blending the bio-crude again with feedstock as well as extracting the solids in each recycling cycle.

Moreover, catalysts could be introduced during liquefaction that would benefit the reaction kinetics. Another prospect would be examining the physical and chemical properties under HTL as well as executing the experiment under different temperature,pressure and time conditions.

The results of this project indicated that the bio-crude needs further upgrading. With all being said catalysts could enhance the quality of the bio-crude either under HTL or Hydrotreatment conditions.

After upgrading, a thorough examination could be introduced in terms of blending with transportation fuels and specifically maritime fuels to investigate if this blending is viable.

Lastly, a thorough assessment of the environmental impacts, including lifecycle analysis,would be beneficial to ensure the sustainability of the co-processing method.

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