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Master’s Programme in Chemical, Biochemical and Materials Engineering

Catalytic upgrading of hydrothermal liquefaction biocrude

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Abstract

The aim of the thesis was to improve the quality of pine biocrude oil by hydrothermal deoxygenation (HDO). The experiments adopted an approach to evaluate the effects of pre-treatment, catalysts, and HDO conditions on crude oil quality. The pre-treatment and HDO together reduced the oxygen content from the original 29.8% to 21.5%-26%. The reduction in oxygen content was accompanied by an increase in higher heating value (HHV), which averaged 31.21 MJ/kg. In the catalyst comparison experiments, the unsulfided Ru/AC, the sulfided Ru/AC, and the sulfided Ni/Mo catalyst performed similarly in terms of crude oil elemental composition. In a comparative test of the catalysts, an average deoxygenation (DOD) of 5.83 % was recorded. The catalysts had very similar impact to the results in terms of elemental composition. Improvements in the optimization of the three variables, temperature, pressure, and time, were not effective and did not show a combination that favored both deoxygenation and high biocrude yield. However, temperature was found to be the most important determinant in the experiments in terms of yield as lower temperature yielded more biocrude. In the optimization of crude oil yields, 320 °C, 5 bar pressure and 4 h reaction time gave the highest yields of 54.4 % and 55.85 % for both mass and carbon balances. The conditions that gave the highest HHV were observed when the reaction took place at 380 °C, 5 bar and over 2 h, giving an HHV of 32.6 MJ/kg and thus the highest oxygen removal. Overall, the difference in HHV and deoxygenation between tests was quite minimal. In catalytic processing, the interaction of the different catalysts is crucial. The work highlights the importance of the balance between temperature, pressure and reaction time, and results in an improved HDO-process to enhance biocrude yield and quality.

Keywords Pine biocrude, black liquor, HDO, hydrothermal liquefaction, hydrodeoxygenation, catalytic upgrading

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Tiivistelmä

Opinnäytetyön tavoitteena oli parantaa männyn bioraakaöljyn laatua hydrotermisellä hapenpoistolla (HDO). Kokeissa käytettiin lähestymistapaa, jossa arvioitiin esikäsittelyn, katalyyttien ja HDO-olosuhteiden vaikutuksia raakaöljyn laatuun sekä saantoon. Esikäsittely sekä HDO yhdessä vähensivät happipitoisuutta alkuperäisestä 29.8 %:sta 21.5–26 %:iin. Hapenmäärän vähennykseen liittyi korkeamman lämpöarvon (HHV) nousu, joka oli keskimäärin 31.2 MJ/kg. Katalyyttien vertailukokeissa, sulfidoimaton Ru/AC,s sulfidoitu Ru/AC , sekä sulfidoitu Ni/Mo katalyytti suoriutuivat samankaltaisesti raakaöljyn alkuainekoostumuksen suhteen. Katalyyttien vertailukokeessa keskimääräinen hapenpoistoksi (DOD) oli 5.8 %. Kolmen muuttujan, lämpötilan, paineen sekä ajan, olosuhdeoptimointi HDO-kokeissa ei ollut tehokasta, eikä parasta mahdollista olosuhteiden yhdistelmää löydetty. Lämpötila todettiin kuitenkin tärkeimmäksi tekijäksi kokeissa. Raakaöljyn saannon optimoinnissa 320 °C:n lämpötilan, 5 baarin paineen ja 4 tunnin reaktioajan avulla saatiin korkeimmat saannot, 54.4 % massa- ja 55.9 % hiilitaseissa. Olosuhteet, jotka antoivat suurimman HHV:n, havaittiin, kun reaktio tapahtui 380 °C:n, 5 baarin ja 2 tunnin aikana, jolloin HHV:ksi saatiin 32.6 MJ/kg ja samalla suurin hapenpoisto. Työssä korostetaan lämpötilan, paineen ja reaktioajan välisen tasapainon merkitystä HDO-prosessissa, jotta biopohjaisen öljyn saantoa ja laatua voidaan jatkossa kehittää.

Avainsanat Mäntyöljy, mustalipeä, HDO, HTL, hapenpoisto, katalyyttinen jalostus

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Experimental part

Preface and acknowledgements

I want to thank my thesis advisors Sari Rautiainen, Juha Lehtonen, and Ville Alopeaus for their advice and guidance.

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Otaniemi, 19.1.2024
Kaarlo Huomo

Symbols and abbreviations

Abbreviations

BL	Black Liquor
BL2F	Black Liquor to Fuel
BLG	Black Liquor Gasification
BLS	Black Liquor Solid
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
CTB	Catalyst-to-Bio-Oil
CUM	Cumulative
DOD	Deoxygenation Percentage
DOE	Design Of Experiments
ER	Energy Ratio
FCC	Fluid Catalytic Cracking
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
GUA	Guaiacol
G	Guaiacyl
HDO	Hydrodeoxygenation
HDT	Hydrotreating
HHV	Higher Heating Value
HTC	Hydrothermal Conversion
HTL	Hydrothermal Liquefaction
HYD	Hydrogenation-dehydration
KF	Karl Fischer (titration)
LHV	Lower Heating Value
LOWESS	Locally Weighted Scatterplot Smoothing
MAT	Micro-Activity Test
MODDE	Model-Oriented Design and Analysis
PL	Precipitated Lignin
PSI	Catalyst provider Compony
Q^2	Predictive Residual Sum of Squares
R^2	Coefficient of Determination
SCWG	Supercritical Water Gasification
TOC	Total Organic Carbon
VGO	Vacuum Gas Oil
VIP	Variable Importance in Projection
VTT	Technical Research Centre of Finland
WSP	Water-Soluble Products

Chemicals

AC	Activated Carbon
BTX	Benzene, Toluene, Xylene
$CaCO_3$	Calcium Carbonate
CHN	Carbon Hydrogen Nitrogen (analysis)
CO_2	Carbon Dioxide
DMDS	Dimethyl Disulfide
IPA	Isopropanol
KL	Kraft Lignin
NaOH	Sodium Hydroxide
Na_2S	Sodium Sulfide
Na_2SO_4	Sodium Sulfate
Ni	Nickel
Ni/Mo	Nickel/Molybdenum
Pd	Palladium
Pt	Platinum
Rh	Rhodium
Ru	Ruthenium

1 Introduction

The use of black liquor, a by-product of the chemical pulping industry, as a source of clean, high-quality biofuel is the focus of the Horizon 2020 project Black Liquor to Fuel (BL2F) [1]. By transforming black liquor into fuel, this project aims to reduce waste and provide an alternative to fossil fuels. The Integrated Hydrothermal Liquefaction (IHTL) process developed by BL2F, launched in April 2020, aims to decrease carbon emissions during fuel intermediate production and enable further upgrading at oil refineries. According to the International Energy Agency (IEA), black liquor is considered the fifth most important fuel on earth, and BL2F aims to contribute to an 83% reduction of CO_2 emissions compared to fossil fuels. An implementation of this project could yield more than 50 billion liters of advanced biofuels by 2050, thereby satisfying the EU demand for advanced biofuels for aviation and shipping. The consortium's efforts could strengthen European leadership in renewable biofuels and contribute to climate protection.

The World Energy Outlook 2019 by the International Energy Agency (IEA) forecasts a 25 % increase in global energy demand between 2018 and 2040, mainly driven by population growth and economic development in non-OECD countries. Fossil fuels are expected to continue to dominate the global energy mix but decline from 81 % (2018) to 74 % in 2040 (Figure 1) [2]. The European Union has proposed directives to substitute conventional non-renewable transportation fuels with high-quality renewable biofuels to reduce greenhouse gas emissions [3]. The biofuels are important contributors in the transport sector, even with the increasing amount of electric cars on the market. According to IEA, with current policies, the demand for biofuels is expected to have an increase of 315 % from 2018 to 2040 [2].

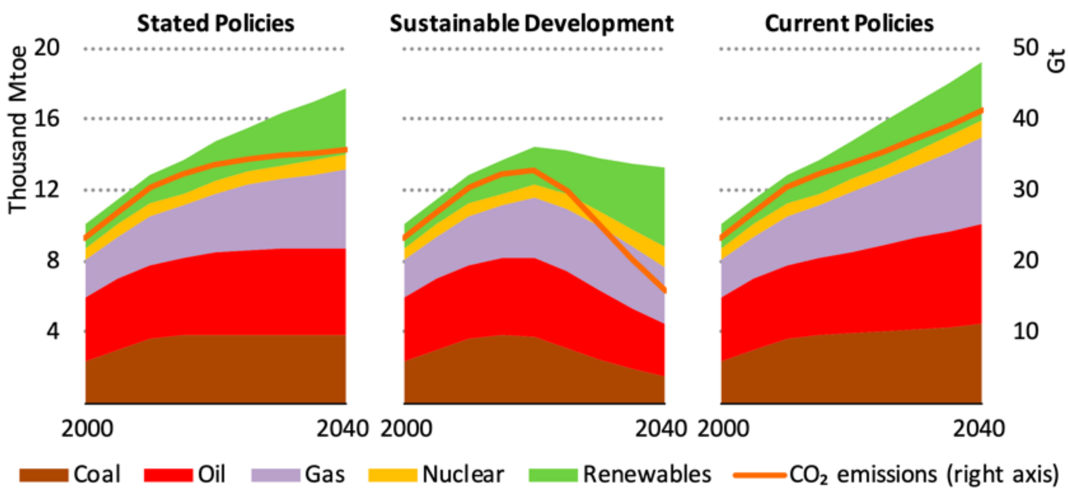


Figure 1. World primary energy demand by fuel and related CO_2 emissions [2].

Biofuel conversion of biomass has become an attractive solution due to environmental concerns, renewability, and reduced emissions compared to fossil fuels [3]. Research is mainly focused on finding high-performance, eco-friendly, alternative second-generation biofuels that can replace conventional fuel [3]. Biofuels are classified into three generations based on their manufacturing process and source materials [4]. The first generation or conventional biofuels are produced from food crops such as sugar, starch, and vegetable oil. These biofuels are primarily manufactured from crops and are currently produced on a commercial scale. Second generation or advanced biofuels are derived from non-food crops and lignocellulosic waste, which require enzymatic digestion, fermentation or for example thermochemical conversion methods to produce biofuels [4, 5]. Third generation, also known as algae based biocrudes, are produced from photosynthetic algae (Figure 2) [4].

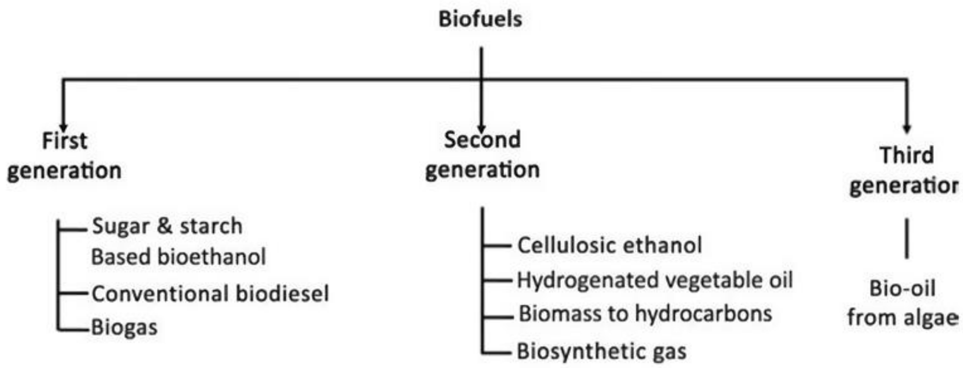


Figure 2. Technological generations of biofuel technology. [4]

The increasing demand for second-generation biofuels has led to the exploration of various bioresources for the production of liquid fuels. Among the biobased waste produced in the European Union, black liquor from the pulp and paper industry is a valuable resource that can be converted to clean biofuels [3, 6]. Black liquor, a by-product from the kraft process, contains residual lignin, hemicellulose, and inorganic chemicals [6]. Although black liquor is used as an energy source in pulp mills, a part of it can be converted into valuable products [6]. Global energy challenges and concerns about climate change have surged interest regarding the production of liquid fuels from lignin through processes such as depolymerization and conversion in a hydrogen-rich environment [7].

Hydrothermal liquefaction (HTL) is an attractive technology for converting the organic fraction of black liquor as it can process wet biomass without drying [6, 8]. The biocrude produced by HTL needs further upgrading and purification, and hydrodeoxygenation (HDO) is a promising technique for removing oxygen from the biocrude [3]. It allows integration of biocrude into standard refinery processes [9, 10]. In this thesis, the potential of using black liquor in HTL biocrude and further processing via HDO for the production of biofuels is explored.

1.1 Aim of thesis

The demand for sustainable fuel sources underlines the criticality of advancing biofuel technologies. This thesis investigates the catalytic hydrothermal hydrodeoxygenation (HDO) of biocrude synthesized from pine HTL biocrude, which is a lignin-rich by-product of the pulp and paper industry. The focus of this study is to investigate the catalytic processes using both sulfided and non-sulfided catalysts and to evaluate their effectiveness in converting biocrude produced by hydrothermal liquefaction into a higher quality biocrude oil. Optimization of operating parameters, namely temperature, pressure, and catalyst selection, can improve fuel quality and process efficiency. By investigating these parameters, the thesis aims to contribute to a new understanding of the HDO process that could advance the viability of bio-crude oil as a greener substitute for conventional fossil fuels.

Research questions

1. Catalyst efficiency and optimization:
    - What are the comparative efficiencies of sulfided versus non-sulfided catalysts in the hydrothermal hydrodeoxygenation (HTHDO) of black liquor biocrude?
    - In the process of catalytic upgrading of hydrothermal liquefaction biocrude, which reaction conditions (temperature, pressure and residence time) optimize the yield and quality of bio-crude oil?
2. Strategies to improve yield and quality:
    - To what extent does the application of hydrodeoxygenation alongside optimized catalytic upgrading parameters improve the yield and quality of biocrude from hydrothermal liquefaction?
    - What are the critical factors along with reaction conditions in the HDO process that most influence the yield and energy density of the resulting biocrude?

2 Kraft lignin and black liquor

In recent years, there has been growing interest in the use of biomass as a source of bioenergy and biofuels due to its potential positive impact on energy optimization and reduction of environmental pollution [6, 11]. The search for sustainable energy sources has led to increased interest in the use of biomass as a means of reducing environmental pollution and optimizing energy consumption. Biomass, such as black liquor generated by the pulp and paper industry, provides an opportunity for the production of valuable co-products [12-16].
The biorefinery concept, which emerged 2002, promises to improve the net efficiency of biomass conversion into energy, reduce costs and reduce greenhouse gas emissions [16, 17]. It is considered a sustainable approach as it uses renewable resources and reduces dependence on fossil fuels [17]. The production of biofuels from biomass is particularly important for achieving a low-carbon future. Biofuels from plant biomass are currently the only sustainable source of liquid fuels.
The implementation of biorefineries can also contribute to the circular economy, where waste materials are converted into valuable products [18]. Biorefineries can convert different types of biomass into value-added products, biofuels and chemicals [19]. This approach is in line with the principles of industrial ecology, which focuses on the sustainable use of resources and the minimization of waste [18].
The main thermochemical conversion methods include pyrolysis, gasification, and hydrothermal liquefaction (HTL) [17, 20, 21]. These technologies are integrated into Kraft pulp mills and have the potential to greatly impact different industrial sectors. In the forestry industry, for example, thermochemical processes such as pyrolysis and HTL are employed to produce biocrude from solid forestry residues, while gasification is used to generate energy from concentrated black liquor [17, 20, 21].
Overall, the biorefinery concept promises to improve net efficiencies for converting biomass into energy, reduce costs, and lower greenhouse gas emissions [16, 17].

2.1 Kraft pulping process

Kraft pulping, a major processing method in the paper industry, primarily breaks down wood biomass into its fibrous components using caustic or acidic solutions to separate cellulose fibers from lignin [22, 23]. It accounts for approximately 90% of global pulp production [24]. Historically, the process was invented by German chemist Carl Ferdinand Dahl in 1879 and has been widely used since then due to its efficiency and robustness [25]. Different pulping methods are represented in Table 1 [26].

Table 1. Commercial pulping methods [26].

	Yield (% of wood)
Chemical pulping	
Kraft, polysulfide kraft, prehydrolysis kraft Soda-antihraquinone (AQ) Acid-sulfide, bisulfite, alkali sulfite-AQ	35–60
Semichemical pulping	
Neutral sulfite semichemical (NSSC) Soda	65-85
Chemimechanical pulping	
Chemithermomechanical (CTMP) Chemigroundwood (CCGWP)	80-90
Mechanical pulping	
Thermomechanical (TMP) Refiner mechanical (RMP) Stone groundwood (SGWP) Pressure groundwood (PGWP)	91-98

The kraft process operates by cooking wood chips under high temperature and pressure using a solution comprising sodium hydroxide (NaOH) and sodium sulfide (Na_2S) [22, 25]. These conditions enable rapid delignification of the wood, producing high-quality pulp while retaining the majority of the cellulose fibers. The primary stages of the kraft process are impregnation, where wood chips are saturated with the alkaline solution, followed by cooking, washing, and screening to refine the pulp [25]. The pulp subsequently undergoes bleaching with agents such as chlorine dioxide and hydrogen peroxide in sequential acidic and alkaline stages, preparing it for shipment to paper mills [22].

One of the significant merits of the kraft process is the potential for chemical recovery. This method has gained popularity due to its fast delignification rate, which results in high-quality pulp, and the possibility of chemical recovery. Approximately 50 % of the initial feedstock is recovered as fiber, while the remaining non-fibrous material is collected in the form of black liquor and concentrated for reuse in the chemical recovery process [27].

Despite its numerous advantages, such as a high pulp yield and superior pulp strength [25, 28], the kraft process does face challenges. It can generate unpleasant sulfur compounds with potential environmental repercussions and requires substantial capital investment for plant establishment [25].

Beyond pulp production, the kraft process yields valuable by-products like kraft lignin (KL), a residue post-delignification [29]. KL offers potential as a feedstock for various products, from biofuels to chemicals and materials [30]. Figure 3 provides an overview of the various technologies that can be integrated with pulp mills for biofuels production [31].

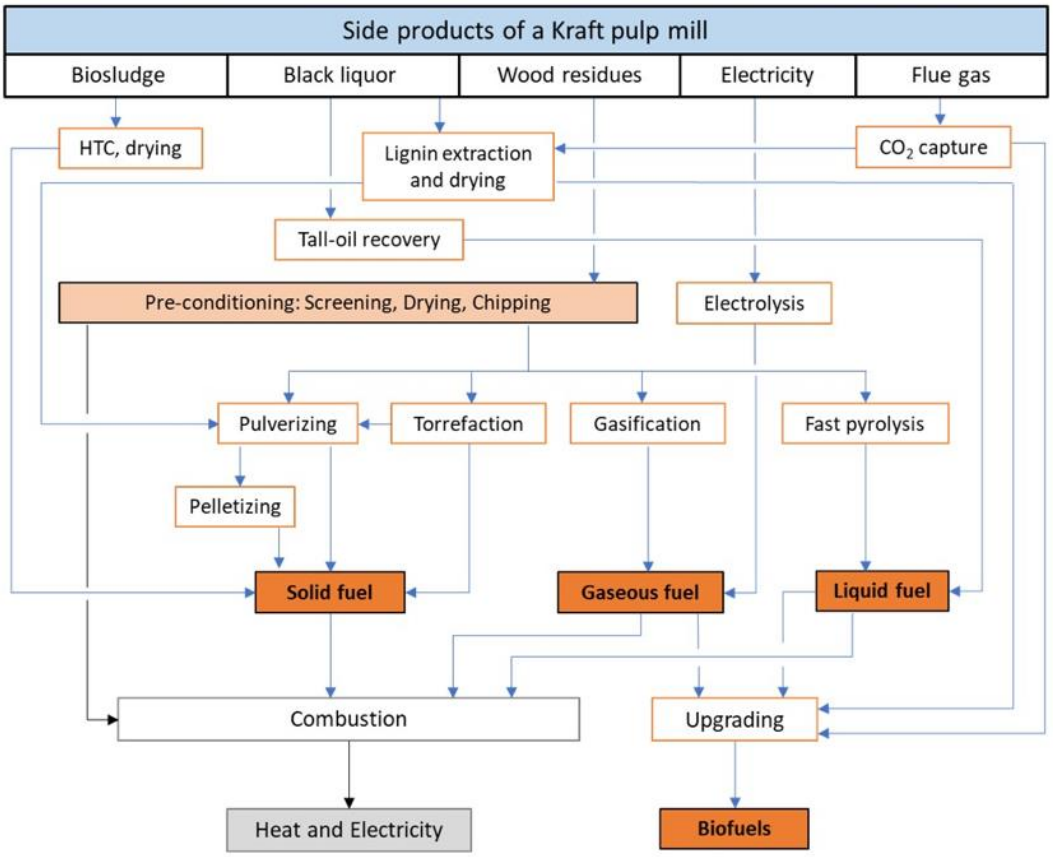


Figure 3. Overview of various technologies integrateable to pulp mills for bio-fuel production [31].

2.2 Black liquor

Black liquor (BL) is a by-product of the kraft pulping process that can serve as the primary ingredient in the recovery process [22]. Despite containing a high percentage of lignin (about 25-30%), its lower heating value per ton (LHV, 12.2 MJ/kg) is relatively low, mainly because of the significant amount of inorganic substances (about 45%) present in it [22]. A conventional pulp mill produces 1.7-1.8 tons dry solids of black liquor per ton of pulp and represents a potential energy of 250-500 MW per mill [16].

The process involves digesting wood chips at high temperature and pressure using white liquor to dissolve lignin, resulting in the creation of BL, which contains inorganic cooking chemicals and combustible material [22]. It is a process liquid produced during the digestion and combustion stages of paper and pulp production, and is composed mainly of lignin, hemicellulose, and other organic compounds [15]. Conventional methods of treatment involve recovery of inorganics and burning of organic matter, which can lead to energy consumption and environmental pollution issues. Estimated black liquor production represented in the Figure 4 [32].

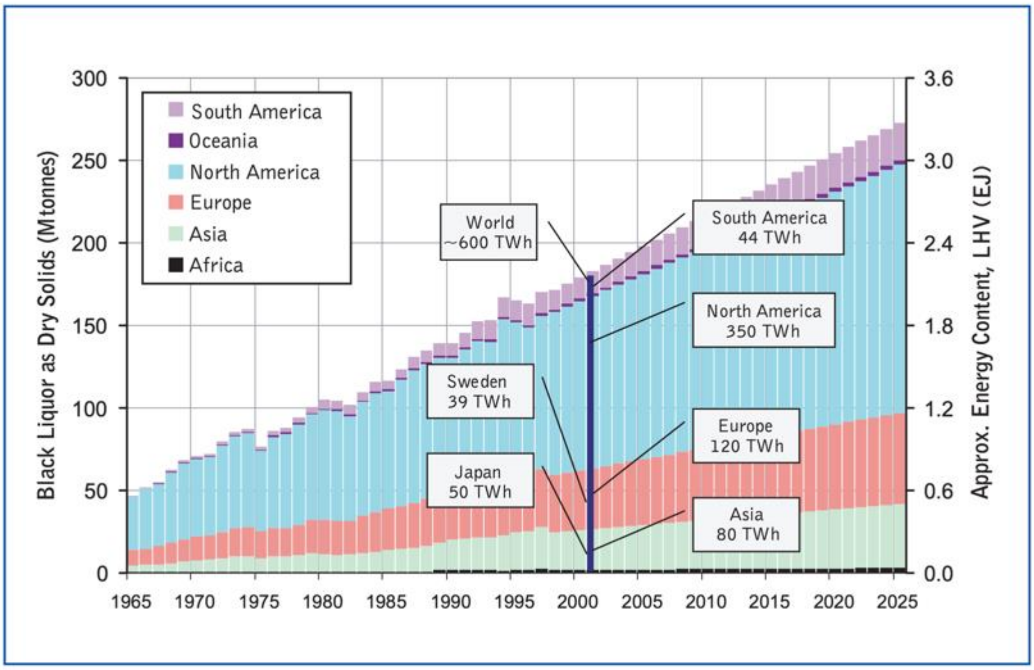


Figure 4. Estimated Black Liquor World production. [32]

The conventional process of recovering cooking chemicals and energy from black liquor is through the use of recovery boilers, also known as the recovery cycle [26, 33]. The recovery boilers are designed to burn the black liquor and recover the inorganic chemicals and energy in the form of steam and electricity [31, 33].

2.2.1 Recovery cycle of black liquor

The process of converting black liquor to energy begins with chemical pulping, in which virgin wood is cooked with sodium compounds, known as white liquor consisting NaOH and Na_2S in high temperature, in order to release the wood fibers from the lignin [6, 34]. The process promotes the breaking of ether bonds between lignin monomers while maintaining the stability of carbon-carbon bonds which leads to the dissolution of the majority of the lignin and a small quantity of cellulose into the water-alkali solution [6].

After cooking, the cooking chemicals and dissolved organics are separated from pulp through washing, while the remaining solution, the black liquor, is transported to a condenser to be evaporated into a concentrated form [33, 34]. The concentrated strong black liquor is then sent to a recovery boiler, typically a Tomlinson model, where it is combusted to produce recoverable thermal energy and an inorganic sodium compound solution, called smelt, that forms green liquor [6]. The green liquor is then converted back to white liquor in the causticizing plant, while the lime kiln decomposes $CaCO_3$ into quicklime and CO_2, which reacts with water to produce calcium hydroxide [6]. The white liquor is then regenerated and returned to the digester [6, 34].

The thermal energy produced by the recovery boiler is used for the evaporation of black liquor and to generate electricity through steam turbines in a process called cogeneration, where waste heat is used to produce steam for the production process and simultaneously generate electricity (Figure 5). [34]

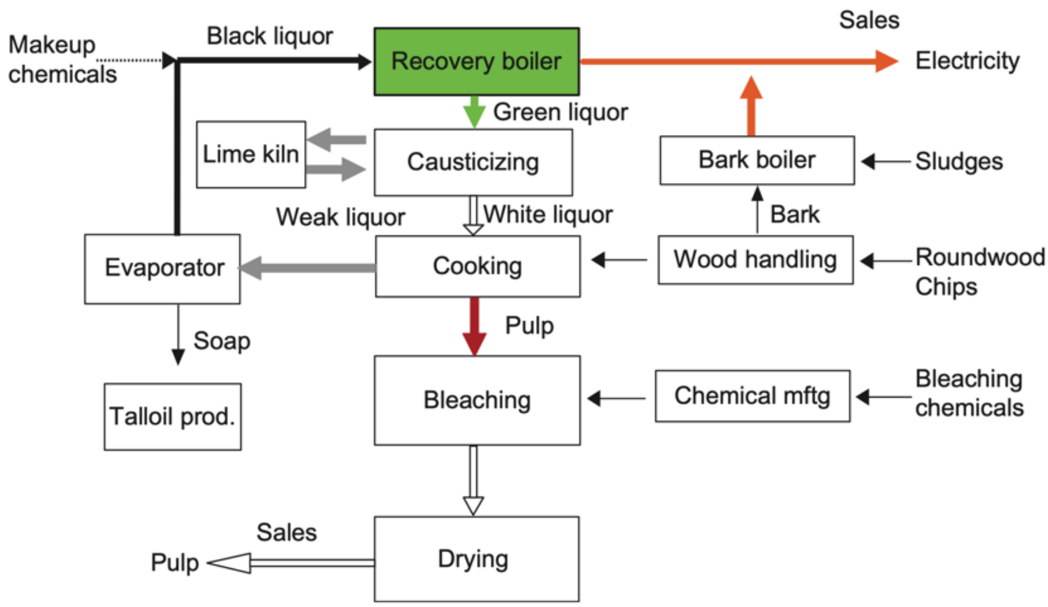


Figure 5. Kraft mill unit operations [33].

Previously, black, alkaline liquor was discarded, but in the 1930s and 1940s, recovery systems for spent liquor were developed and widely adopted due to new equipment and increased mill size. Recovering black liquor is more cost-effective than purchasing new chemicals and has the added benefit of producing energy when burned, which can cover all internal mill use in modern pulp mills. [33]

The recovery boiler is a key component in the pulp and paper industry that operates based on the principle of burning concentrated black liquor [33].

This liquor is a mixture of water, organic dissolved wood residue, and chemicals used to remove lignin from cellulose fibers. The combustion of the organic portion of the black liquor generates heat that is utilized to produce high-pressure steam. The steam is then expanded in a turbine to generate electricity, and the low-pressure steam is used for process heating applications within the mill. During combustion, sulfur compounds are released, and the recovery boiler captures them through a reaction between sodium and the sulfur compounds. This reaction produces sodium sulfate (Na_2SO_4) and carbonate, which are then used to regenerate the pulping chemicals to sodium sulfide (Na_2S). Optimal process conditions are required to minimize sulfur gas emissions. The recovery boiler process consists of several unit operations, including the combustion of black liquor, the generation of steam and electricity, and the regeneration of pulping chemicals. It plays a crucial role in the efficient utilization of resources and the sustainability of the pulp and paper industry.

Key points of the recovery cycle [33]:

- Thermal oxidation of organic compounds in black liquor to generate high-pressure steam for energy production.
- Reduction of inorganic sulfur compounds, such as sodium sulfate, to sodium sulfide through combustion in the recovery boiler.
- Conversion of the molten inorganic flow, mainly consisting of sodium carbonate and sodium sulfide, into weak white liquor to form green liquor through dissolution.
- Recovery of inorganic dust from flue gas through filtering and other processes to prevent loss of valuable chemicals.
- Production of sodium fume by reaction with combustion residue of released sulfur compounds to capture the sulfur as a solid by-product.

2.2.2 Composition of black liquor

Black liquor is a by-product of the pulping process in the paper industry. It is a complex mixture of organic (2/3rd) and inorganic (1/3rd) compounds [35, 36]. The organic content of black liquor includes lignin, polysaccharides such as hemicellulose and cellulose, and extractives such as fatty acids and resin acids [35]. On the other hand, the inorganic part of black liquor consists of compounds such as sodium hydroxide, sodium sulfide, sodium carbonate, sodium thiosulphate and sodium chloride (Table 4) [6, 35, 36].
Black liquor contains a substantial amount of lignin and residual pulping salts. Table 2 provides the properties of black liquor from softwood and hardwood sources, which shows that the contents of solid, lignin, and ash can vary significantly [6]. This variability is due to the amount of water used in the pulping process and the stage of evaporation at which the black liquor

samples were collected in commercial operations [6, 35, 37]. The elemental composition represented in the Table 3.

Table 2. Composition of softwood weak black liquor (dry matter basis) by two kraft pulp mills [6].

Origin	**Country**	**Density (kg/m3)**	**Total Dry solids (g/L)**	**Total Hemicelluloses (g/L)**	**Total Lignin (g/L)**	**Ash (g/L)**	**Sodium**
Softwood (unknown) Black liquor	Sweden	1095	183	3.56	63.8	84.3	37.8
Softwood (Pine) Black liquor	Finland	1128	218	3.6[a]	56.3	un-known	28.8

Table 3. Elemental composition of dry pine black liquor (dry matter basis) [6].

C	**H**	**O**	**N**	**S**	**Na**	**K**	**Cl**
wt. %	**wt. %**	**wt. %**	**wt. %**	**wt. %**	**wt. %**	**wt. %**	**wt. %**
38	3.6	33.1	0.1	4.8	19.1	0.9	0.2

Table 4. Weight fractions of inorganic compounds in black liquor (dry matter basis) [6].

Na_2S	Na_2SO_2	$Na_2S_2O_3$	Na_2SO_3	**NaOH**	Na_2CO_3	**Other**
wt. %	**wt. %**	**wt. %**	**wt. %**	**wt. %**	**wt. %**	**wt. %**
17	12	14	7	6	32	12

The composition of black liquor can vary depending on the raw material used in the pulping process (Table 5) [6, 36]. Hardwoods tend to have more methoxyl groups in the lignin, while softwoods have more hydroxyl groups [35]. The presence of ionized groups, such as carboxylic or phenolic groups, in lignin is responsible for its solubility, which is highly dependent on pH [36]. Lowering the pH can lead to precipitation of lignin [35]. Changes in pH can also affect the viscosity of the black liquor.

Table 5. Black liquor elemental composition of different lignocellulosic materials [36, 38].

Element	Hardwood	Softwood	Bamboo	Bagasse	Straw
Oxygen	32–39	32–39	33–34.1	33–36.4	32–34
Carbon	31–37	32–37.5	32–34.5	34–36.9	32–36.6
Sodium	16–23	17–23	17.5–19	18–19	16.5–17.5
Sulfur	3–7	2.9–7	3–4	2–3	1.5–2.5
Hydrogen	2.9–3.9	3.2–4.5	2.5–3.5	3–4	3.5–4.5
Potassium	1–9	1.5–3.7	3–4.5	0.5–1.2	1.5-3
Chlorine	0.1–3.5	0.1–3.3	1–3	0.2–1	1–3
Nitrogen	0.14–0.6	0.05–0.015	0.2–0.8	0.2–0.6	0.2–1.2
Inert	0.1–0.3	0.1–2	0.1–1	0.1–1	0.1–1

Black liquor poses challenges in terms of toxicity and disposability, since it contains a multitude of organic compounds, including dioxins, furans, and polycyclic aromatic hydrocarbons (PAHs), some of which are carcinogenic and mutagenic to aquatic organisms [35]. It has high values of biological oxygen demand (BOD) and chemical oxygen demand (COD), as well as the presence of toxicants such as chlorophenols and high color units. The color of the black liquor is primarily due to lignin and its derivatives and polymerized tannins, which are recalcitrant in nature due to the presence of carbon-carbon biphenyl bonds. To address these challenges, various methods have been developed to detoxify black liquor, including fungal treatment, photocatalysis, enzyme treatment, adsorption, and overliming [35, 36].

Lignin

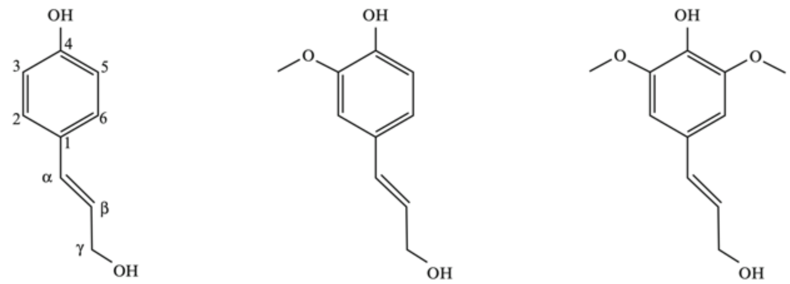
As previously mentioned, lignin is a major molecule found in black liquor, a by-product of the pulp and paper industry [39]. Lignocellulosic biomass, which includes lignin, presents a sustainable and abundant source of energy and carbon for the production of fuels and chemicals [40]. Lignin is a complex, three-dimensional polymer that is the second most abundant organic material on Earth, following cellulose, and accounts 15-40% of the dry mass fraction in woody plants [39, 40]. It binds with cellulose and hemicelluloses, and together they form the cellular structures of plant cell wall structures [39].

Lignin can be classified into three main categories: lignosulphonate, kraft lignin, and organosolv lignin [39]. Lignosulphonate is the most prevalent type and accounts for 88% of lignin, while kraft lignin constitutes 9% and organosolv lignin 2% [39]. These categories display structural differences in the degree of methoxylation at the 3' or 3'-5' position of phenolic rings, based on the origin of the biomass utilized [39].

Lignin, a highly branched and substituted mononuclear aromatic biopolymer that binds together with cellulose and hemicelluloses to form plant cell wall structures [17]. It is one of the three major components of lignocellulosic biomass, and typically accounts for 15–40 % of the dry mass fraction in woody plants. Lignin is a high molecular weight, three-dimensional, and heterogeneous macromolecule consisting of many phenylpropanoid units, which are the oxidative polymerization products of three types of hydroxycinnamyl alcohol sub-units (monolignols). These sub-units include p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) phenylpropanoid units, with structural differences in the extent of methoxylation at the 3′ or 3′–5′ position of phenolic rings, depending on the source of the biomass, and can be used to differentiate between different types of lignin (Figure 6) [17, 41, 42]. Approximately 100 million tons of lignin was produced in 2015 and was valued at USD 732.7 million, and the value is estimated to reach $913.1 million by 2025 [40]. It is suggested that annual production of lignin could increase to 225 million tons, partly due to an increase in biofuel production.

Structure of monolignols

4-hydroxyphenyl (H) | Guaiacyl (G) | Syringyl (S)



Source	Content (%, *w/w*) [8]		
Softwood lignin	-	90-95	5-10
Hardwood lignin	-	50	50
Grass lignin	5	75	25

Figure 6. Three sub-units of lignin and their relative content in lignocellulosic biomass [41].

3 Thermochemical conversion and refining of black liquor

Thermochemical processes are a diverse array of thermal and chemical conversion technologies for transforming and utilizing biomass into various forms of energy and valuable chemicals [43]. Thermochemical biomass processes such as pyrolysis or gasification, which typically use biomass such as dry wood as a feedstock [44]. Thermochemical process can be called hydrothermal when executed with excess of water at high temperature and pressure. Thermochemical conversion routes presented in the Figure 7 [5].

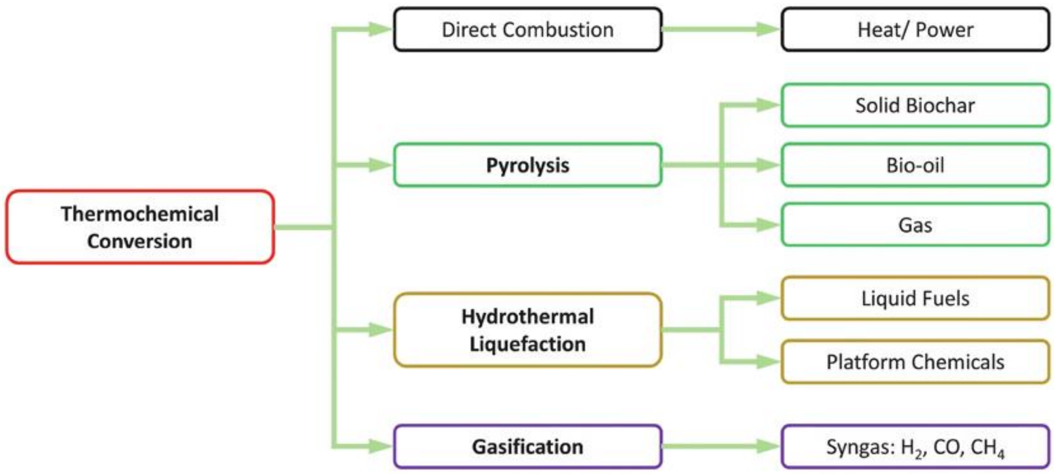


Figure 7. Thermochemical conversion routes for biomass utilization (modified from source) [5].

3.1 Hydrothermal liquefaction of black liquor

Hydrothermal liquefaction (HTL) is a promising thermochemical conversion pathway for producing biocrude from various feedstocks [16, 45]. Liquefaction constitutes a method in which lignocellulose undergoes depolymerization and partial deoxygenation, resulting in biocrude formation [46]. The yield of biocrude generated via HTL varies generally between 24 and 64 % [47]. HTL has been applied to various types of biomass, including cornstalk, bamboo, and sewage sludge, to produce fuel and chemicals at different temperatures (220-400°C) and pressures (50-250 bars) with a residence time of 5-120 minutes [16, 45, 48].

The reaction parameters, such as temperature, pressure, residence time, and the reaction environment, can affect the yield and distribution of the products (Figure 8). The main contents of biocrude produced through HTL are alcohol, ketone, and phenolic compounds. The reaction process is complex and heavily dependent on the characteristics of the raw material [16]. Different biomass sources may result in different phenolic compound ratios [48].

The process utilizes the unique properties of water in its sub- and supercritical state, such as low viscosity and high solubility for organic compounds, to break down the biomass and produce biocrude with minimal tar production and high energy efficiency [16, 45]. Under these conditions, water is an excellent medium for conducting homogeneous reactions [45]. The basic mechanisms of HTL involve depolymerization, decomposition, and recombination of biomass molecules. HTL process holds a lot of potential for the sustainable production of biofuels and chemicals from biomass.

Research has been carried out with the addition of capping agents, such as formic acid, phenol, isopropanol, and ethanol, to enhance the yield of phenolic compounds in the biocrude by reducing unwanted side reactions [49]. Metal catalysts, such as Ni, Co, ZrO, and mesoporous catalysts, have also been employed to increase the yield of the biocrude [49]. Depending on the suitability of the catalyst the yield can be increased by 50 to 60% [47]. The catalyst increases the flow properties of biocrude and lowers the biocrude heteroatom content [47].

Studies have shown that thin black liquor and low concentrations of kraft lignin are crucial for high yields of phenolic compounds in the biocrude [50]. However, the main challenge with HTL is the high temperature and dilute concentration requirements, which lead to material corrosion and economic challenges [49]. A second hydroprocessing step is also required to obtain a fuel. Despite these challenges, HTL is a promising technology due to its ability to produce phenolic compounds that can be easily separated from the water phase in one step.

High energy efficiency of HTL process makes it a suitable alternative to other conversion processes such as pyrolysis. The HTL process also produces small amounts of tar and highly reactive oxygenated compounds in the form of carbonyls, phenols, fatty acids, and alcohols [45]. These compounds require further upgrading through catalytic processes to produce high-quality biofuels. Catalytic upgrading of HTL oil involves the removal of unwanted compounds, such as N-heterocyclic compounds and aromatic organometallic complexes, to produce biofuels with higher energy content.

3.1.1 Properties of HTL biocrude

HTL biocrude results in a dark, viscous biocrude that has an energy value between 70-95% of petroleum fuel oil [8]. The biocrude obtained from HTL consists of a range of products, including long-chain fatty acids, nitrogenated and oxygenated heterocyclics, and long-chain hydrocarbons. The chemical compositions of HTL biocrude produced from black liquor are presented in Table 6.

Table 6. HTL oil properties produced from black liquor by autoclave with a heating time of 3 h, reaction time of 45 min in a temperature of 350 °C, and cooling time of 4 h. Sample 1 containing both NaOH (10 wt %) and glycerol, and sample 2 only NaOH [8].

biocrude	**water**	**carbon**	**hydrogen**	**sulfur**	**oxygen**	**ash**	**HVV**
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	MJ/kg
Sample 1	21.9	54.6	7.2	3.1	23	11.7	24.9
Sample 2	31.3	48.6	7.2	3.0	29	12.4	22.0

The biocrude also contains heteroatoms such as nitrogen and oxygen that must be removed through mechanisms such as decarboxylation, decarbonylation, denitrogenation, and hydrodeoxygenation (HDO) to refine the biocrude into diesel-like fuels [51]. While research has been conducted on the upgrading of HTL products such as amino acids, fatty acids, and carbohydrates, there is still limited knowledge on the catalytic conversion of mixtures of these molecules and the impact of nitrogen heteroatoms on catalytic upgrading.

According to a study (Duangkuew et al. 2023), where black liquor was converted into various products through high-temperature liquefaction (HTL), achieved an overall conversion rate above 80% for all conditions tested. Biocrude and biochar yields were determined and compared for different temperatures and gas environments. In the article (Duangkaew et al. 2023), the reaction environment is significantly influenced in the yield of biocrude. Under atmosphere pressure, liquefaction was found to be highest at 300 °C with N_2 resulting in a conversion of 38 % and with H_2 in a conversion of 42 %, making the hydrogen more efficient in terms of yield [48].

The presence of hydrogen appeared to promote the production of biocrude, possibly due to the hydrogenation of phenolic compounds in lignin with the remaining acid catalyst (H_2SO_4) [48]. At higher temperatures (400°C), biocrude yield decreased due to thermal cracking and depolymerization of the oil. On the other hand, the yield of biochar was higher at lower operating temperatures for both gas environments. For both gas environments, biomass conversion increased with increasing temperature, likely due to the preferred hydrolysis and depolymerization of the lignin structure at high temperatures.

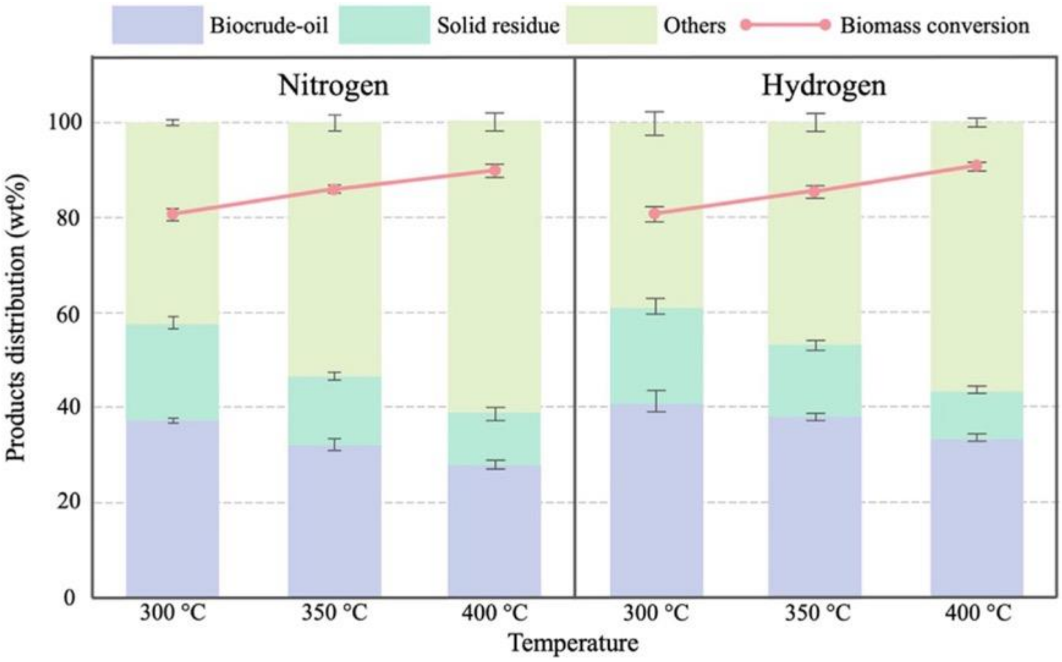


Figure 8. Effect of temperature and gaseous environment on the product distribution of hydrothermal liquefaction of black liquor received from pulp and paper company [48].

The distribution of chemical species in the same article by Duangkuaew et al. (2023) varied with operating temperature and gas atmosphere (Figure 9) [48]. At 400 °C under hydrogen atmosphere, biocrude contained the lowest content of phenolic compounds (66.04 %), with ketones (29.64 %), long chain hydrocarbons (3.19 %), and alcohols (1.13 %) being the other major constituents. The phenolic compound content reached a maximum value of 81.92 % at 300 °C, and decreased to 73.06 % and 66.04 % as the temperature increased to 350°C and 400°C, respectively. The depolymerization and decarboxylation reactions increased with the operating temperature. The major phenolic compounds found in biocrude were phenol, cresol, 2-methoxy-phenol, 2-methoxy-4-propyl phenol, 4-ethyl-2-methoxy Phenol, and 4-Ethyl-2,6-dimethoxyphenol. The presence of hydrogen in the reaction system resulted in higher amounts of phenolic compounds compared to the nitrogen atmosphere due to bond cleavage by the hydrogenation and hydrogenolysis reactions.

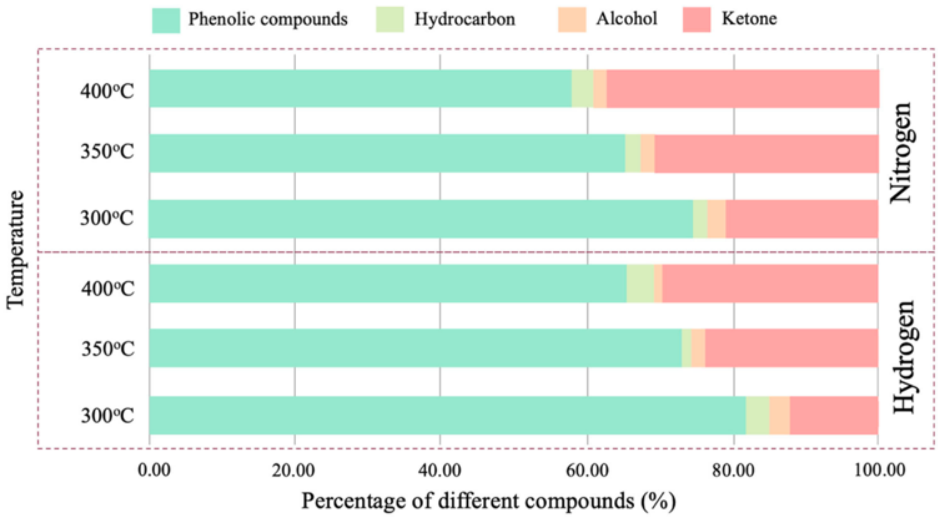


Figure 9. Percentage of various product categories chart of Biocrude oils distribution under different conditions of hydrogen and nitrogen after HTL of black liquor received from pulp and paper company [48].

A study about hydrothermal conversion (HTC) was conducted by Zhao et al. (2020) where they examined the production of phenolics and hydrochar from black liquor solid (BLS) and precipitated lignin (PL) under varying conditions [52]. Optimal conditions for biocrude production were determined by testing different temperatures, holding times, and reaction solvents. The highest biocrude yield of 53.3% was obtained for BLS using a 50 wt% ethyl acetate/water cosolvent at 300°C for 30 min, while PL yielded 86.7% using a 50 wt% ethanol/water cosolvent under the same conditions. GC-MS analysis confirmed that phenolics were the primary products in biocrude, with H-type phenols dominating in BLS and S-type phenols in PL.

3.1.2 Catalyst use in HTL

The influence of the catalyst on the products of hydrothermal liquefaction (HTL) can be complex and multifaceted. Catalysts can have significant effects on various outputs of the process, resulting in variations in both the quantity and quality of the produced biocrude [47, 53]. One crucial goal of catalysis is to maximize the yield of biocrude, while minimizing the production of other reaction products such as char, gases, and water-soluble compounds. The amount of produced biocrude is essential for determining the economic feasibility of the process.

Another objective of catalysis is to improve the quality of biocrude by reducing the amount of oxygen, nitrogen, and other heteroatoms present in the product, which can facilitate its upgrading with lower efforts. The higher heating value (HHV) can be used to quantify the degree of improvement in product quality [53]. HHV can be calculated theoretically by using a formula developed by Channiwala & Prakih (2002) (1) [54]:

$$\mathrm{HHV} = 0{,}3491 \times \mathrm{C} + 1{,}1783 \times \mathrm{H} + 0{,}1005 \times \mathrm{S} - 0{,}1034 \times \mathrm{O} - 0{,}0151 \times \mathrm{N} - 0{,}0211\mathrm{A} \tag{1}$$

An increase in HHV is directly related to a reduction in the number of heteroatoms. Tendencies of improving both yield and improving HHV do not necessarily occur simultaneously, making it difficult to evaluate the effectiveness of catalysis. Nonetheless, a successful catalytic process should aim to increase the proportion of biomass energy that is converted into biocrude. This can be measured by the energy recovery (ER), which is defined as in the Eq. (2) [53, 55]:

$$\mathrm{ER} = \frac{\mathrm{Y_{biocrude}} \cdot \mathrm{HHV_{biocrude}}}{\mathrm{HHV_{feed}}} \times 100\% \tag{2}$$

The energy recovery ER is defined as the ratio of the mass yield of biocrude ($\mathrm{Y_{biocrude}}$) obtained from the hydrothermal liquefaction (HTL) process, to the higher heating values (HVV) of both the produced biocrude and the biomass feedstock, both on a dry ash-free basis ($\mathrm{HHV_{biocrude}}$ and $\mathrm{HHV_{feed}}$). [53] The choice of catalyst greatly impacts the yield of biocrude. Studies have shown that the use of alkali catalysts, such as K_2CO_3, Na_2CO_3, and KOH, result in a significant increase in biocrude yield, containing lignocellulosics and nitrogen containing feedstocks [47, 53]. However, the use of some acid catalysts, such as sulphuric acid, can result in a decrease in yield (15%) [47]. The use of organic acid catalysts like acetic acid and formic acid shows higher biocrude yield, but these acids have found to be consumed during the reaction [47]. Heterogeneous catalysts have also shown promising results compared to homogenous catalysts [47]. Overall, the choice of catalyst is a crucial factor in determining the yield of biocrude through HTL [47]. The effect of homogeneous and heterogeneous catalyst on biocrude yield in HTL is represented in the Table 7 and Table 8. [53]

Table 7. Effects of homogenous catalysts on biocrude yield, carbon, and HHVs [30].

Feedstocks	Temp (°C)	Catalyst	Non-Cat-Yield (%)	Cat-Yield (%)	Change in Yield by (%)	Change in C by Value (%)	Change in N by Value (%)	Change in HHV by Value in (MJ/kg
Wood (birch-wood saw-dust)	300	K_2CO_3	19	38	100.00	−4.00	−0.03	−3.00
Wood (birch-wood saw-dust)	300	KOH	19	39	105.26	−5.00	0.00	−3.00
Wood (birch-wood saw-dust)	300	$FeSO_4$	19	32	68.42	−4.00	0.03	2.00
Wheat Straw	350	K_2CO_3	26	32	23.08	2.61	−0.19	0.54
Wheat Straw	400	K_2CO_3	24	23	−4.17	−1.18	0.27	−0.47
Bio-pulp	350	K_2CO_3	28.9	36.6	26.64	1.24	−0.09	0.80

Table 8. Effects of heterogeneous catalysts on biocrude yield, carbon, and HHVs [30].

Feedstocks	Temp (°C)	Catalyst	Non-Cat-Yield (%)	Cat-Yield (%)	Change in Yield by (%)	Change in C by Value (%)	Change in N by Value (%)	Change in HHV by Value in (MJ/kg
Wood (birchwood sawdust)	300	MgO	19.00	30.00	57.89	−5.00	0.03	−2.00
Wood (birchwood sawdust)	300	hydrotalcite (HT)	19.00	34.00	78.95	−7.00	0.00	−5.00
Wood (birchwood sawdust)	300	Colemanite	19.00	36.00	89.47	−3.00	0.00	−2.00
Wood (birchwood sawdust)	300	HT/KOH	19.00	36.00	89.47	−6.00	0.02	1.00

According to a study (Chang, et al. 2016), when bamboo chopsticks were subjected to hydrothermal liquefaction (HTL) with the addition of K_2CO_3 catalyst, the resulting biocrude yield improved significantly, reaching up to 21.2 wt% at a temperature of 290°C, as compared to only 3.8 wt% in a non-catalytic experiment [56]. Additionally, the higher heating value (HHV) of the biocrude increased to 31.6 MJ/kg [56]. Moreover, in a study (Arturi, et al. 2017) where kraft lignin was subjected to hydrothermal liquefaction (HTL) with the addition of K_2CO_3 catalyst at a temperature range of 280–350 °C, the use of the catalyst led to an increase in the yield of liquid products while decreasing the formation of char. The catalyst was also found to enhance the yield of monomeric aromatics produced during the HTL process. [57]

Castor residue
A factorial design model was used to determine the optimal conditions for obtaining the maximum biocrude yield in catalytic HTL of castor residue with alkali catalysts. Temperature, time, and catalysts were identified as the main factors, and a maximum total biocrude yield of 21.20 wt% was obtained at 300 °C, 60 min, and 0.5 M K_2CO_3. [58]

Lignin
For catalytic HTL of lignin was investigated the use of Ni–Al/MCM-41 series catalysts, and the Ni–Al/MCM-41 catalyst gave the maximum biocrude yield of 56.2 wt% [59]. The reaction mechanism of lignin HTL was proposed, in which the alcoholic solvent produces active hydrogen and methoxy ($-OCH_3$) and ethoxy ($-OC_2H_5$) radicals that cleave the ether C–O–C (ß-O-4) bond to generate aromatic compounds.

Catalytic hydrothermal liquefaction (HTL) has a more complex reaction system than pyrolysis [5]. Studies on the mechanism of catalytic HTL have mainly focused on the impact of reaction parameters on product distribution, biocrude composition and quality resulting from various catalytic HTL reaction pathways.

3.2 Gasification of black liquor

Gasification is a thermochemical conversion process in which biomass feedstocks are subjected to high temperature partial oxidation or steam reforming [60]. These intense process conditions result in products with a relatively simple chemical structure, but with a wide range of applications. Typical gasification products include hydrogen, carbon monoxide and dioxide, and light hydrocarbons. Some gasification processes use catalytic or bio-conversion methods, which produce mainly methane and carbon dioxide as product gases. These products have a wide range of applications, including energy production and chemical synthesis. Potential polygeneration steps for gasification of black liquor represented in Figure 10.

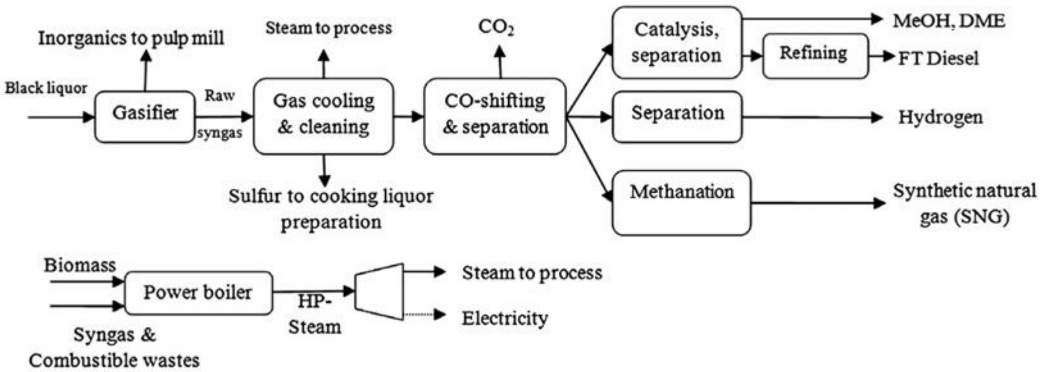


Figure 10. Potential polygeneration of biofuels from black liquor in kraft pulp mill [22].

By using gasification technology, black liquor can be converted to syngas [49]. The Black liquor gasification (BLG) process can be integrated into the pulp mill to increase energy self-sufficiency, co-produce pulp and valuable energy products such as methanol and dimethyl ether, and potentially convert a kraft mill into a biofuel supplier [49]. The gaseous effluent arising from the process comprises a mixture of various chemical species, including carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), and nitrogen (N_2) (in the case of air being employed as the oxidant). However, this mixture may also contain unwanted impurities, such as minute char particles, ash, tars, and oils. The solid remnants remaining after the process is complete are primarily comprised of ash, which is principally composed of the oxides of calcium (Ca), potassium (K), sodium (Na), magnesium (Mg), and silicon (Si). Additionally, carbon or char may also be present in the solid residue. [61]

Table 9. Reactions identified during gasification [38].

Reactions	Reactants/ reactions	Products
Pyrolysis and Tar cracking	Biomass and tar	C, CO, H_2, CO_2, C_2H_4, tar
Homogeneous gas-gas reactions		
Combustion	$CH_4 + O_2$	CO, H_2
Steam reforming	C_2H_4/CH_4 + CO2	
Water Gas Shift	CCO + H_2O	CO_2, H_2
Heterogenous reactions		
Carbon oxidation	C + O_2	CO_2
Partial oxidation	C + O_2	CO
Boudourd reaction	C + CO_2	
Water-gas reaction	C + H_2O	CO, H_2

3.2.1 Supercritical water gasification

Supercritical water gasification (SCWG) provides a method of producing hydrogen from wet biomass at temperatures lower than typical gasification processes [44]. Its unique feature is the use of supercritical water, which makes it efficient for wet biomass without drying. This technique is particularly advantageous because it bypasses energy-intensive steps such as black liquor evaporation in the Kraft process, thereby improving energy efficiency [62].

In SCWG, the water in the biomass acts as both a solvent and a reactant, aiding the water-gas shift reaction and producing a high H_2 yield [29]. For the process to be effective, it's run at high pressures to retain the water and prevent it from evaporating. Typically, the best dry matter content is around 20 wt% or less, depending on the type of biomass. A challenge with SCWG is the significant heat required to heat the feedstock to close to 600°C. However, this can be overcome with heat recovery systems. From an environmental perspective, SCWG has shown advantages in life cycle assessments, but needs to be optimized for better energy consumption and cost efficiency [29].

According to a study by Casademont et al. (2020) on supercritical water gasification (SCWG) of black liquor (BL), the simultaneous production of hydrogen and disposal of organic waste was investigated. The experiments were carried out in a continuous reactor with short residence times at temperatures between 600-700 °C and pressures of 230 bars [46]. In this study, the best hydrogen yield was obtained at 700 °C and 24.5 s residence time. The highest chemical oxygen demand (COD) removal was also obtained under these conditions.

3.3 Pyrolysis of black liquor

Pyrolysis is a thermal depolymerization technology that has been widely utilized to convert biomass into biofuels and chemicals. In this process, biomass is heated in the absence of oxygen at temperatures between 300 to 600 °C [63]. Different components of biomass (cellulose, hemicelluloses, and lignin) are pyrolyzed at different rates by different mechanisms and pathways [64].

Pyrolysis can be classified into two categories: slow pyrolysis and fast pyrolysis. Slow pyrolysis yields char as the primary product, whereas fast pyrolysis generates liquid, commonly known as pyrolysis oil or biocrude, with up to 70% yield for lignocellulosic biomass [63, 64]. To achieve high biocrude yields, it is essential to promptly heat the biomass (usually >100 °C/s) and rapidly cool the volatiles to produce the biocrude product. Fast pyrolysis takes less than two seconds and requires control of the moisture content of the dry biomass to below 10% and finely ground biomass feedstock. The biocrude and solid char generated can serve as fuel, and the gas can be recycled into the process. In comparison, slow pyrolysis does not require fine feedstock particle size and usually operates with lower heating rates and longer residence times [64]. A careful reactor design is also essential to ensure a minimum temperature gradient within the reactor.

Thermal depolymerization of lignin to aromatics and other value-added products through fast pyrolysis is of great interest as the production capacity of second-generation biofuels increases [63]. Biocrude, derived from lignocellulosic biomass, is a complex mixture of various organics such as anhydrous sugars, aldehydes, ketones, acids, furans, and phenols [63]. Among the various pyrolysis methods, fast pyrolysis is particularly attractive for its simplicity, scalability, and biocrude processing efficiency. Biocrude produced in pyrolysis can be distilled into biofuels and chemicals. Biochar produced in slow pyrolysis is a multifunctional material, useful as a fuel, soil conditioner, or activated carbon precursor.

Peng et al. (2014) conducted pyrolysis of kraft black liquor at various temperatures (300–500 °C) and obtained biocrude compounds (tar) with yields of 50 wt% and 27 wt% for char and gas phases, respectively. Higher pyrolysis temperatures resulted in higher concentrations of H_2, CH_4, and CO in the gas phase and a decrease in CO_2 [65].

Catalytic pyrolysis of black liquor was investigated by Heeres et al. (2018), and the conversion of bio-aromatics using in-situ or ex-situ catalytic pyrolysis with zeolite catalysts. The Ga-modified H-ZSM-5 catalyst produced the highest yield of BTX (7 wt%), with slightly higher yields for hardwood black liquors compared to softwood. Additionally, the content of aromatic compounds with methoxyl groups decreased, while intermediate compounds with fewer methoxyl groups increased [66]. Pyrolysis is a promising technology in the conversion of kraft lignin to fuels, with limited studies being done precisely to black liquor [49].

3.4 Comparison of existing thermochemical processes and pathways

Liquefaction and pyrolysis are two major techniques used for the production of biocrudes. The oils produced through pyrolysis are water-soluble and have a higher content of oxygen compared to the oils produced through liquefaction [17]. Liquefaction process takes place at a temperature range of 250-325 °C and pressures of 50-200 bars, whereas pyrolysis process occurs at a temperature range of 375-525 °C and pressure of 1-5 bars [17]. Pyrolysis is a cheaper method compared to liquefaction, and many pyrolysis techniques are being used in commercial production. Unlike liquefaction and pyrolysis, gasification converts solid biomass mainly into a combustible gas mixture (syngas), while pyrolysis and liquefaction convert biomass into liquid products [5]. The temperature exceeds them also with a range of 500-1200 °C [5].

There are several primary methods for converting kraft lignin into fuels [49]. These include gasification followed by Fisher Tropsch, which results in linear hydrocarbons. Hydrothermal liquefaction produces phenols, which can then be converted into aromatic compounds through hydrotreatment. Hydrocracking can also be used to produce phenolics, which can then be transformed into hydrocarbons through hydrotreatment. Another approach involves esterification, followed by hydrotreatment, which produces aromatic compounds from lignin. The thermochemical mechanisms are summarized in Figure 11 [5, 49, 62].

In summary, biofuel and biocrudes can be produced from a variety of sources including agricultural waste, forest waste, black liquor, and wood [17]. The production process involves a reactor, which can convert up to 50-90% of biomass energy into a liquid. These biocrudes can contain a complex mixture of more than 400 different compounds such as alcohols, esters, ketones, acids, aldehydes, and aromatic compounds. Although biocrudes are commercially used as boiler fuel for stationary power and heat production, they can be converted into more high value products such as biofuels. To utilize biocrudes as transportation fuels, they need to be upgraded, which is further discussed in following chapter 4. The thermochemical technologies are summarized in Table 10 [5, 49, 62].

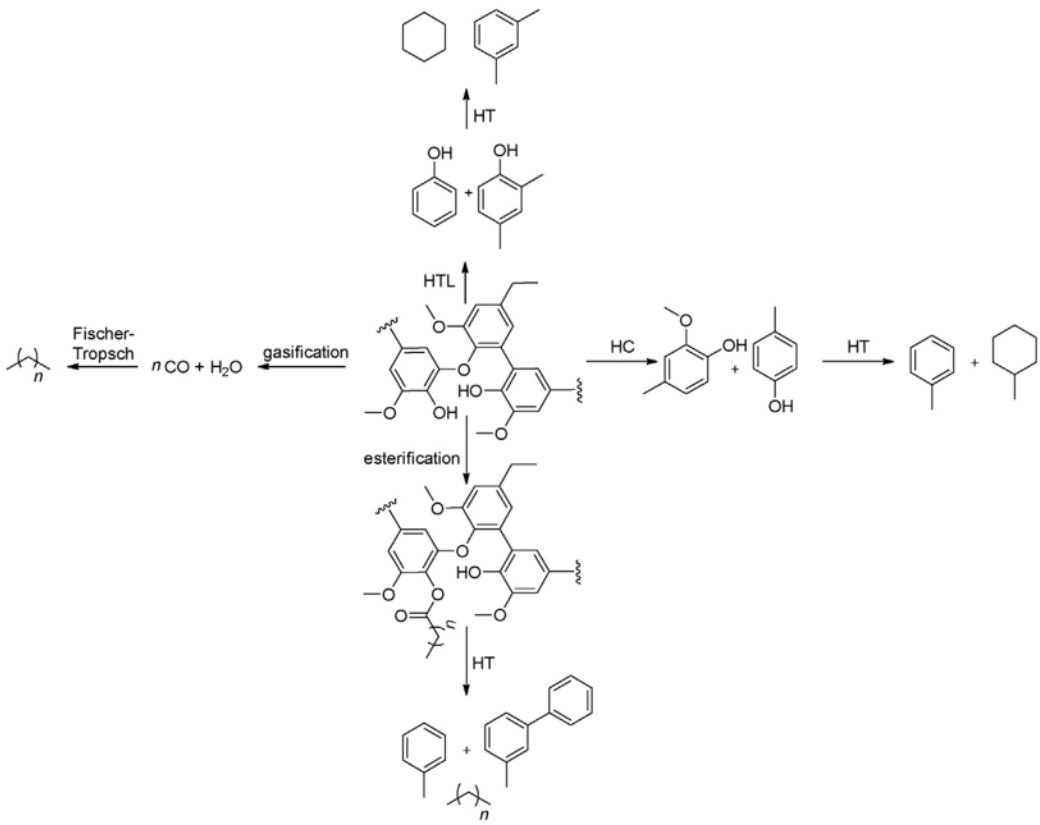


Figure 11. Main routes for conversion of kraft lignin to fuels: gasification followed by Fisher Tropsch to give linear hydrocarbons; hydrothermal liquefaction to produce phenols followed by hydrotreatment to give aromatic compounds; hydrocracking to produce phenolics followed by hydrotreatment to give hydrocarbons; esterification followed by hydrotreatment to give aromatic compounds from lignin [49].

Table 10. Thermochemical treatments of kraft black liquor [5, 62].

Treatments	Operational Parameters	Main products	Summary	Ref.
Pyrolysis	Heavy/dried kraft black liquor			
Slow pyrolysis	<500 °C	Biochar	- Slow pyrolysis is characterized by long residence times and low to moderate temperatures, with a focus on maximizing char production [67].	[5]
Fast pyrolysis	400-550 °C	Biocrude & gas	- Fast pyrolysis involves rapid heating of biomass to moderate to high temperatures with a very short residence time, optimized for the production of a liquid product (bio-oil) [67].	[5]
Flash pyrolysis	550-750 °C	Biocrude	- Flash pyrolysis is a rapid thermal decomposition process that involves the instantaneous heating of a material to high temperatures, resulting in the production of various products such as biochar, bio-oil and other organic compounds [68, 69].	[5]
Hydrothermal	Inert atmosphere Weak craft black liquor			
Hydrothermal liquefaction (HTL)	250-370 °C 40-350 bars	Biocrude Biofuel	- Uses water at high temperatures and pressures to convert wet biomass into biocrude [70]. - The biocrude produced from HTL can be further upgraded by processes such as hydrotreating to remove oxygen and sulfur [71]. - Use of organic solvents result in the production of more phenolic compounds, organic acids and alcohols [62]. - These processes work on different feedstocks and catalysts can improve the quality and yield of biocrude [72-75]	[5]
Hydrothermal carbonization (HTC)	180-250 °C 20-100 bars	Hydrochar	- Uses water at high temperatures and pressures to convert wet biomass into biochar [70]. - Char can be revalorized, but commonly used as fuel [62]. - Carbonized lignin can be recovered.	[5]
Gasification	500-1200 °C [5]			
Gasification	Heavy/dried kraft black liquor 600-1000 °C	Syngas (H_2, CH, CO, CO_2)	- Thermochemical process that converts biomass into syngas, a mixture of carbon monoxide, hydrogen and other hydrocarbons, through partial oxidation at high temperatures [76]. - Direct gasification is autothermal [62]. - Recirculation of inorganic compounds to the conventional recovery Process.	[62]
Hydrothermal gasification (SCWG)	Weak Kraft black liquor 375-750 °C >221 bars	Syngas Liquid fraction	- Can produce gas through an autothermal process that avoids the evaporation stage [62]. - Kraft black liquor can be used as alkaline catalyst. - Partial removal of sulfur	[5, 62]

4 Catalytic upgrading of HTL biocrude via HDO

Hydrotreatment of HTL biocrude through hydrodeoxygenation (HDO) has gained interest due to its ability to improve biocrude quality by increasing cetane number (ignition value), heating value (energy content) and reducing oxygen content [77]. HDO involves the reaction of biocrude with hydrogen in the presence of a catalyst, typically a metal catalyst such as platinum or nickel [78]. This breaks down the heteroatom-containing compounds and converts them into more stable hydrocarbons [78]. The process is energy-intensive, and high temperature and pressure can cause coking or carbon deposition on the catalyst surface, affecting catalytic activity [77]. There are various approaches or strategies that can be used to modify the reaction.

Catalytic upgrading of HTL biocrudes has been extensively studied, identifying different challenges for different feedstocks [74]. Various types of organic materials pose different challenges to overcome during hydrotreating. This results in variations in the removal of heteroatoms and in the types and compositions of the products targeted. The selection of catalysts for HDO reactions is also dependent on the specific requirements of the biocrude and the desired product. For instance, a hydrodesulfurization catalyst have been used to reduce the sulfur content primarily.

Reaction conditions such as temperature, pressure, flow rate of hydrogen and duration of reaction are significant factors which have the potential to impact both the efficiency and selectivity of the HDO process [79]. In the hydrodeoxygenation of biomass, the use solvents such as protic ionic liquids as solvents has been shown to enhance the selectivity towards biofuels derived from lignin [80].

Hydrodeoxygenation of biocrudes is a challenging process due to the production of water from the reaction itself and the presence of water within the HTL biocrude, which can lead to deactivation of the catalysts [81]. However, in some cases the presence of water in the reaction system can improve the hydrodeoxygenation activity of certain catalysts [82]. General table comparing the elemental composition and other properties of HDO, HTL and flash pyrolysis products in Table 11 [17].

Table 11. Properties of non-upgraded and upgraded biocrudes [17].

	Hydrothermal liquefaction	Flash pyrolysis	Hydrodeoxygenated biocrudes
Elemental analysis			
carbon (wt %)	72.6	43.5	85.3-89.2
hydrogen (wt %)	8.0	7.3	10.5-14.1
oxygen (wt %)	16.3	49.2	0.0-0.7
sulfur (wt %)	<45	29.0	0.005
H/C atom ratio (dry)	1.21	1.23	1.40-1.97
Density (g/mL)	1.15	24.8	0.796-0.926
Moisture (wt %)	5.1	24.8	.001-0.008
Higher heating value (MJ/kg)	35	22.6	42.3-45.3
Viscosity	15,000 (61 °C)	59 (40 °C)	1.0-4.6 (°C)
Aromatic/aliphatic carbon	-	-	38/62—22/78
Research octane number (RON)	-	-	77
Distillation range (wt %)			
IBP-225 °C	8	44	97-36
225-350 °C	32	Coked	0-41

4.1 Catalyst use in HDO

4.1.1 Catalyst concept

Catalysis is a kinetic phenomenon that involves the acceleration of reactions and the lowering of activation barriers, rather than changing equilibria [83-85]. In catalysis, reacting molecules bind to the catalyst, react to form a product, and then leave the catalyst available for the next reaction sequence [83]. Catalysis involves the adsorption of reactants onto the surface of the catalyst, where they react to form products that desorb and leave the surface free for the next reaction event. Catalysts offer energetically favorable pathways for both forward and reverse reactions and can improve the selectivity of the desired conversion. Catalysts enable reactions to proceed faster, reduce costs, and improve product yields. Figure 12 illustrates how the use of a catalyst reduces the activation energy required for a chemical reaction.

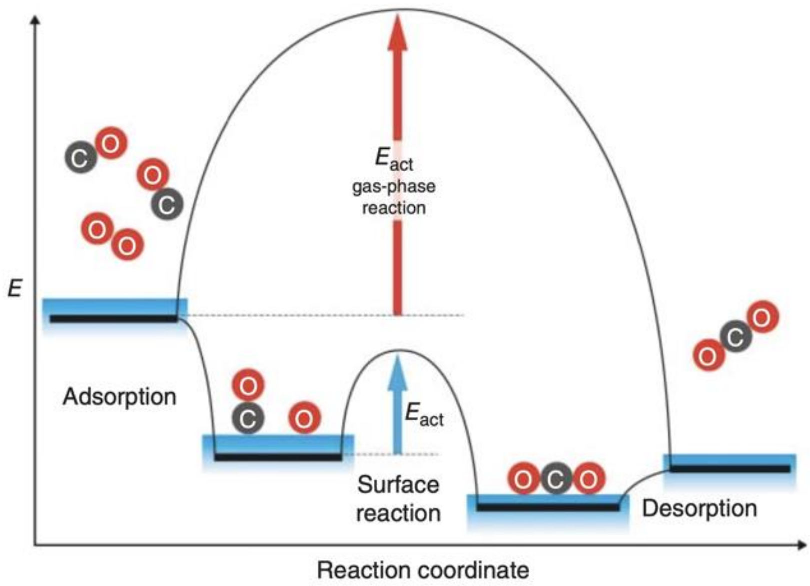


Figure 12. Potential energy scheme of a heterogeneously catalyzed reaction: the CO oxidation [84].

Heterogeneous catalysis

Heterogeneous catalysis is a subfield of catalysis that involves the use of a catalyst in a different phase from the reactants [84, 85]. This means that the catalyst is usually in a solid form, while the reactants are either gaseous or liquid. Heterogeneous catalysts play a critical role in the chemical industry and are often composed of metal nanoparticles. The surface area of the catalytic metal particles can be increased by dispersing them finely across the surface of a support material. This not only increases the number of active sites but also alters the surface structure and electronic properties of the nanoparticles, improving their catalytic performance.

The most common support materials for heterogeneous catalysts are porous metal oxide materials such as alumina, silica, titania, zirconia, graphite, and activated carbons, with surface areas ranging from 10 to >1000 m2/g [84, 85]. Support materials should be thermally, mechanically, and chemically stable because they are used in chemical reactors. The interaction between the support and the nanoparticles of the active phase should be strong enough to stabilize the nanoparticles against sintering but not too strong to adversely affect the catalytic properties of the nanoparticles.

The structure of heterogeneous catalysts can be described on four length scales: atomic, (sub)micron, mm scale, and reactor scale [84]. The atomic level of the surface of nanoparticles determines the intrinsic kinetics of catalytic reactions. The morphology and porosity of the support are usually defined on a (sub) micron scale, whereas the size of the support particles typically varies between 10 µm and 1 cm. Heterogeneous catalysis finds applications in the manufacture of chemicals, production of fuels, and providing environmental protection [84]. The major reactions and common catalysts used in the reactions are represented below in Table 12.

Table 12. Largest processes based on heterogeneous catalysis [85].

Reaction	**Catalyst**
Catalytic cracking of crude oil	Zeolites
Hydrotreating of crude oil	Co–Mo, Ni–Mo, Ni–W (sulfidic form)
Reforming of naphtha (to gasoline)	Pt, Pt–Re, Pt–Ir
Alkylation	H_2SO_4, HF, solid acids
Polymerization of ethylene, propylene, a.o.	Cr, TiClx/$MgCl_2$
Ethylene epoxidation to ethylene oxide	Ag
Vinyl chloride (ethylene + Cl_2)	Cu (as chloride)
Steam reforming of methane to CO + H_2	Ni
Water-gas shift reaction	Fe (oxide), Cu–ZnO
Methanation	Ni
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO3	Pt–Rh
Acrylonitrile from propylene and ammonia	Bi–Mo, Fe–Sb (oxides)
Hydrogenation of vegetable oils	Ni
Sulfuric acid	V (oxide)
Oxidation of CO & hydrocarbons (car exhaust)	Pt, Pd
Reduction of NOx (in exhaust)	Rh, vanadium oxide

4.1.2 Hydrotreatment and HDO

Industrial hydrotreating (HDT) catalysts, which are commonly used in the petroleum industry for desulfurization of fuels, typically comprise a molybdenum sulfide (or tungsten sulfide) phase promoted by cobalt or nickel and are usually supported on alumina [86]. Alumina is the most commonly used support due to its excellent textural and mechanical properties, it has been recognized that it is not an inert carrier, and the promoter ions Co and Ni can react with the support and occupy sites in the external layers, resulting in changes in the catalyst's structure and activity.

Hydrodeoxygenation process (HDO) research encompasses the performance of metal catalysts [87]. The examination of HDO reaction attributes involves the analysis of reaction mechanisms, reaction kinetics, and product structure [87]. In a similar vein, research pertaining to metal catalyst performance entails the assessment of product yield, conversion, selectivity, catalytic efficiency, and interactions between metal and electronic components [88]. Catalysts in hydrodeoxygenation (HDO) with good “H-H” dissociation ability and “C-O” and “C=O” adsorption and activation abilities are needed to ensure superior deoxygenation performance [77]. Optimal production processes and suitable catalyst systems are crucial for the production of the desired products.

The conversion of oil in HDO is dependent by the effects of catalyst support, promoters, and active component-support interactions on HDO activity and selectivity, as well as details about the reaction mechanism [77]. By optimizing the active components and controlling the properties of the support, the HDO performances of the corresponding catalyst can be effectively improved. The choice of metal active component depends on the model compound or biocrude, which determines the deoxygenation pathway.

Sulfided $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ are the prevalent catalysts used for hydrotreating catalytic hydrodeoxygenation (HDO), due to their low cost, selectivity, and impurity tolerance [81, 89]. Some metals including Co, Re, W, Mo, and Fe have a stronger affinity to O atom and exhibit better performance for hydrodeoxygenation [90]. To prevent deactivation of sulfided catalysts by sulfur release in the absence of replenishment, a sulfiding agent is often added to maintain their activity and stability, as biomass and biocrudes contain little sulfur [3, 89]. The elimination of sulfur is needed in the final fuel product due to requirements [91].

4.1.3 Support selection in HDO

Support selection is crucial because active sites, such as oxygen vacancies, acid and basic sites, can catalyze reactions like C-O dissociation and C-C, C-O hydrogenation and alkylation [90]. Too strong acidic sites, on the other hand, may lead to cracking of long-chain alkanes. Conventional supports include metal oxides like Al_2O_3, ZrO_2, SiO_2, TiO_2, CeO_2, and Nb_2O_5, acidic micro- and mesoporous molecular sieves like SAPO-11, HZSM-5, MCM-22, and SBA-15, and reducible supports like CeO_2, WO_3, and TiO_2 [90]. Innovative composite materials are also used as supports, including CaO-MgO mixed oxide and HZSM-5 introduced to Pt/C catalyst [90]. Noble metal catalysts supported on various materials can serve as potential alternatives to conventional hydrotreatment catalysts, as they do not rely on sulfur to maintain their activity [92, 93]. Furthermore, these catalysts have demonstrated the ability to remove carbonyl groups from fatty acids and esters and oxygen from phenols.

4.1.4 Deactivation in HDO

In addition to activity and selectivity, the stability of a catalyst is an important consideration in catalytic applications [85, 94]. Catalyst deactivation can occur for a number of reasons and one possible cause is a kinetic phenomenon [95]. This can happen when an intermediate species reacts to produce a substance that acts as a poison for the active sites of the catalyst [96]. Such poisoning can be caused by processes such as oligomerization or coke formation, but it can also be caused by specific poisons that adsorb strongly to the catalyst and block the active sites, preventing the catalytic cycle from continuing [96, 97]. Two main deactivation mechanisms in hydrotreating represented in Table 13.

Table 13. Typical cases of catalyst deactivation in Hydrotreating and the measures taken to counteract it [97].

Catalyst	Main deactivation mechanism	Time scale of deactivation	Consequences for catalyst	Regeneration
Co/Mo/S/Al_2O_3	Coke	Months	Once-through catalyst	Coke combustion
	Metal sulfides	Days	Adapted porosity	-

4.1.5 Catalytic mechanism of lignin based HTL biocrude in HDO

According to Kim et al. (2019) the hydrodeoxygenation (HDO) mechanism of biomass-derived oxygenates over heterogeneous catalysts proceeds through the adsorption of oxygenates onto the catalyst surface, followed by the dissociative adsorption of hydrogen onto the surface to form surface hydrogen species. These surface hydrogen species then react with the adsorbed oxygenates, leading to the removal of the oxygen atom and the formation of water. The resulting intermediate can undergo a series of reactions, including hydrogenation, dehydrogenation, and dehydration, leading to the formation of hydrocarbon products. The specific HDO mechanism may vary depending on the type of oxygenate and catalyst, reaction conditions, and catalyst preparation method. [98]

The removal of oxygen from phenolic compounds via hydrodeoxygenation (HDO) occurs via three pathways: a) direct deoxygenation (DDO), b) hydrogenation-dehydration (HYD), and c) keto-enol tautomerization [99]. DDO involves direct cleavage of the C(sp2)-OH bond, whereas HYD first hydrogenates the aromatic ring before dehydrating the C(sp3)-OH bond. Tautomerization-deoxygenation involves the tautomerization of phenolic compounds to a keto-enol equilibrium mixture, followed by hydrogenation of the

keto group and dehydration to produce deoxygenated aromatics. The choice of pathway is influenced by factors such as metal catalyst, support, temperature and hydrogen pressure.
DDO and tautomerization-deoxygenation produce deoxygenated aromatics, while HYD produces deoxygenated cyclic compounds [99]. DDO is preferred because it consumes less H_2, avoids hydrogenation and produces high octane products, although it requires higher reaction temperatures. The complexity of the mechanism increases in the order of DDO < HYD < tautomerization, with HYD having the highest H_2 consumption and the strongest temperature and hydrogen pressure dependence. An example reaction mechanism pathway in HDO presented in Figure 13 below.

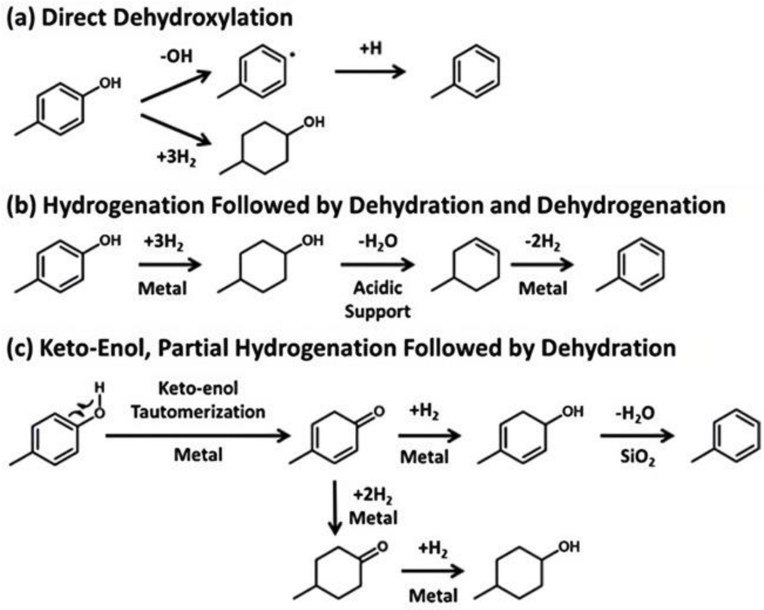


Figure 13. Proposed HDO Mechanisms of Phenolic Compounds in the Literature [99].

For the black liquor based HTL oil, which is derived from a high amount of lignin, the focus in conversion of content should be on aromatic compounds such as phenolics, high oxygen containing products. The main lignin monomer is guaiacyl (G) in softwood, hardwood, and grass-based biomass [41]. Guaiacyl refers to a range of phenolic compounds that have a methoxy group attached to a phenyl ring, such as guaiacol (GUA), syringol and vanillin, making them similar from their structure [88]. Structures of phenolic model compounds represented in Figure 14.

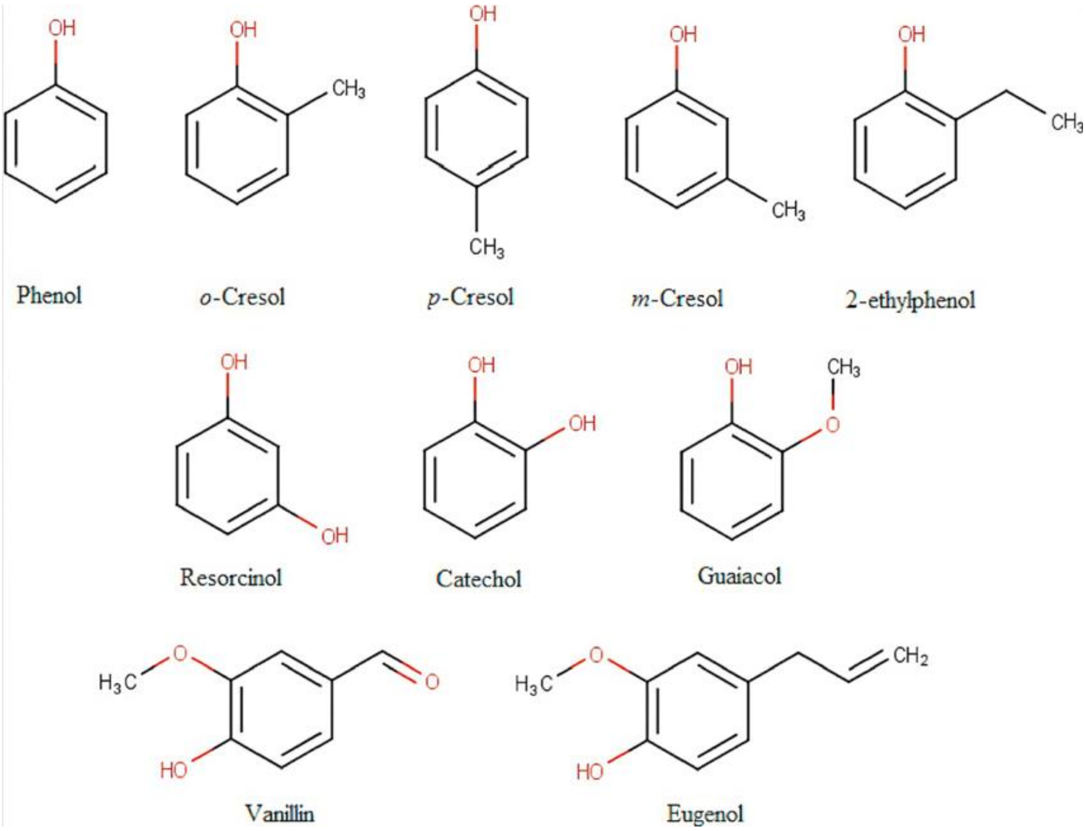
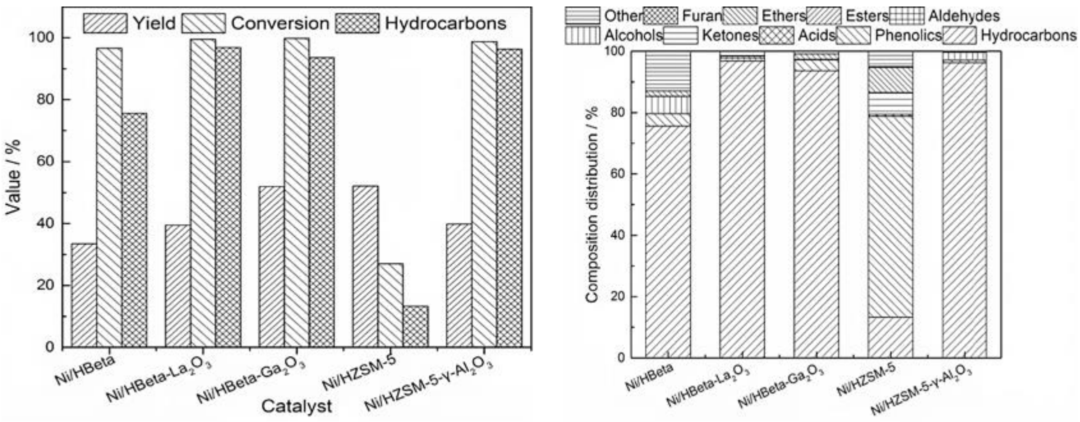


Figure 14. Molecular structures of phenolic model compounds [88].

The HDO pathways for GUA, acetic acid, and hydroxyacetone involve transmethylation, isomerization, hydrogenation, self-condensation, demethylation, aldol condensation, and saturated hydrogenation to produce cyclic and aromatic hydrocarbons or long-chain alkanes [87]. According to Li et al. (2020), the hydrodeoxygenation (HDO) of biocrude model compound GUA for hydrocarbon fuel was investigated utilizing Ni-based catalysts that were modified with metal oxides (Al, La, and Ga). The study revealed that mixed supported catalysts, including Ni/HZSM-5-γ-Al2O3, Ni/HBeta-La2O3, and Ni/HBeta-Ga2O3, could generate hydrocarbons, with hydrocarbon content of over 70.65% when utilized for the HDO of guaiacol (GUA). Among the tested catalysts, Ni/HZSM-5-γ-Al2O3 was the most effective for the HDO of acetic acid and hydroxyacetone. The hydrodeoxygenation of GUA with different catalyst mixtures and the content value as well as composition distribution are represented in the Figure 15.



(a) (b)

Figure 15. The impact of nickel-based catalysts on the hydrodeoxygenation (HDO) of guaiacol (GUA) can be described: (a) the effectiveness of the HDO process, and (b) the constituents found in the resulting liquid products [87].

4.2 Process conditions in HDO

Hydrodeoxygenation (HDO) involves elevated hydrogen pressure at moderate or high temperature in the presence of a heterogeneous catalyst to lower the oxygen content [100].

4.2.1 Temperature

The rate of a chemical reaction typically increases with an increase in temperature, although this relationship is more complex in catalysis. The Arrhenius equation describes the temperature dependence of the rate constant for elementary reactions (Eq. (3)) [85]:

$$K(T) = ve^{-E_a/RT} \qquad (3)$$

Where T represents the temperature, v is the preexponential factor, E_a is the activation energy (kJ mol-1), and R is the gas constant [85].

The equation shows that the rate constant increases exponentially with decreasing activation energy. This means that a reaction with a lower activation energy will have a higher rate constant and thus a faster reaction rate than a reaction with a higher activation energy. In the context of the catalyst, the lower activation energy provided by the catalyst allows the reaction to proceed faster, as it provides an alternative pathway with a lower energy barrier [85]. This leads to a lower activation energy for the reaction and an increased reaction rate.

According to Bu et al. (2013), the temperature is a critical factor that affects the hydrodeoxygenation process during lignin-derived phenols conversion. The temperature range for hydrodeoxygenation varies quite a lot (150-500 °C) depending on the type of catalyst and feedstock used, but is typically between 200-350°C [7]. Although higher temperatures generally result in higher conversion rates, they can also lead to unwanted side reactions and lower product yields. Moreover, higher temperatures can cause lower selectivity for desired products and higher amounts of undesirable by-products. Conversely, lower temperatures can result in longer reaction times and lower conversion rates but may lead to higher selectivity and yields of desired products. Because of this, the selection of the optimal temperature for hydrodeoxygenation is crucial and requires a careful balance between these factors.

4.2.2 Pressure

Hydrodeoxygenation of biocrudes involves the use of high-pressure H_2 and heterogeneous catalysts to treat biocrudes at moderate temperature for the removal of sulfur, nitrogen, and oxygen from petrochemical feedstocks [17]. The pressure can have a significant impact on the HDO process outcome, including yield, purity, and reaction time. In general, higher pressures tend to increase the yield of hydrocarbon products while decreasing the selectivity for certain product types. For example, at high pressures an increase in selectivity can be seen. According to Luo et al. (2016) the selectivity of (HDO) reactions strongly depends on the hydrogen pressure, likely due to changes in the hydrogen surface coverage. The HDO process involves the oxygen in the biocrude reacting with H_2 to form water and saturated C-C bonds [17]. The objective is to avoid hydrogenation of aromatics in the biocrudes since this decreases the octane number and increases H_2 consumption.

4.2.3 Time

The deoxygenation process can be influenced by the amount of catalyst and the reaction time. According to Remon et al. (2019), the conversion of the model compound guaiacol to HDO was improved by increasing the reaction time [101]. However, in another study by Kong et al. (2021) in HDO of guaiacol, it was observed that the total yield of liquid products reached a maximum at 30 min and then showed a decreasing trend with increasing reaction time [102]. It would be logical to assume that extending the reaction time may enhance the degradation of lignin, resulting in an increase in biocrude formation, but the formation of other undesirable compounds and the decrease in yield must be taken into account when optimizing the time as well.

4.2.4 Supercritical water in HDO

Supercritical water has been extensively researched for its potential benefits in the hydrodeoxygenation (HDO) of biocrude or oil [103]. The use of supercritical water at high temperatures has been shown to lead reduce the nitrogen and oxygen content of the oil, a reduction in sulfur content, and an improvement in the higher heating value of the bio-oil [104]. There can be drawback to supercritical conditions. For instance, according to Seehar et al. (2020) , it could lead to a decrease in biocrude yield due to the polymerization of macromolecules into gaseous formations or solid residues [105]. In addition, the high water content typical to this method could also lead to catalyst deactivation, mainly due to the loss of sulfur [106].

Recent study investigated the impact of the supercritical phase on nine reactions involving various types of compounds, with a focus on validating a supercritical water model and exploring its potential for upgrading heavy aromatic compounds from lignocellulosic biomass [107]. The results showed that favorable conversion of aromatic compounds to less oxy-functional compounds in the supercritical conditions at a temperature range of 427-500°C and a total pressure of 250-463 bars.

Catalyst use in supercritical water
The lack of stability in a catalyst is a problem in supercritical water when performing hydrothermal HDO [81]. Ni catalysts has only been successful at low temperatures and in the presence of additional acid catalysts. The noble metals such a Pt and Pd supported on activated carbon are shown to be active for 6 hours in HDO in the presence of water over a short period of time, but the stability in longer reactions is unknown. The high cost of the noble metals motivates the search for more economical, stable, and selective catalyst options for high temperature and pressured HDO reactions including water. According to Dickenson et al. (2014), the use of supercritical conditions has several advantages, such as preventing catalyst poisoning and enabling rapid mass transfer of gasses, including H_2 produced by in-situ decomposition of formic acid in the feed solution.

4.3 Research of biomass based HTL oil in HDO

In this chapter, a few essential articles are examined to see which factors are the most important in hydrotreatment, more specifically in HDO. The articles are summarized and then analyzed for the background of this thesis. In particular, the effect of catalyst type and quantity is important. The temperature conditions and their optimization and the overall final composition of the oil.

4.3.1 Recent study of black liquor based HTL oil in HDO

The study by Melin et al. (2022) aimed to produce (a) hydrothermal liquefaction (HTL) biocrude from kraft black liquor, (b) perform alkaline metal salt removal, (c) eliminate oxygen and reduce molar weight via hydrodeoxygenation, and (d) execute catalytic cracking with vacuum gas oil (VGO) to create second generation transportation biofuel [8]. The potential of coprocessing of hydrodeoxygenated biocrudes produced from kraft black liquor through hydrothermal liquefaction (HTL) was investigated.

The HTL process was optimized to lower the oxygen content of the biocrude, and the addition of glycerol during the process and washing was found to improve biocrude quality [8]. In the HDO biocrudes performed with black liquor-based HTL biocrude, the depolymerization of lignin and the oxygen content was further lowered.

To produce HDO biocrudes for coprocessing experiments, two steps were carried out. First, kraft black liquor underwent hydrothermal liquefaction (HTL) to depolymerize lignin and reduce oxygen content [8]. HTL yielded bio-oil with monomeric phenolic compounds and lowered the oxygen content from 40% to 10-20%. The 23-29 wt% oxygen content was still too high for coprocessing, making another hydrodeoxygenation step necessary to further reduce the oxygen content to 5-10 wt%. Glycerol addition during HTL improved biocrude quality by acting as a radical scavenger, preventing repolymerization and reducing char yield. Washing with sulfuric acid removed sodium salts and decreased ash content, which negatively impacted the HDO step and risked deactivating the FCC Y-zeolite catalyst during coprocessing.

A high deoxygenation level proved advantageous for transforming refined crude oil into gasoline components. By maintaining a 10 wt % pre-treated biocrude ratio during coprocessing, naphtha yields remained high at 45%, with minimal change in coke yield [8]. This outcome is encouraging, as naphtha is the primary target in fluid catalytic cracking (FCC). The properties of HTL oil after the HDO process and the monomer content from the hydrodeoxygenation are shown in Table 14 and Figure 16.

Table 14. Properties after HDO performed from black liquor-based HTL oil with sample 1 being at 250 °C, 100 bar H2 pressure, 6 h reaction time and 10 wt % of 10Ni10Co/H-ZSM-5 catalyst, and sample 2 at an increased 367 °C, with similar conditions otherwise [8].

Biocrude	**H_2O**	**carbon**	**hydrogen**	**nitrogen**	**sulfur**	**oxygen**	**ash**
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
Sample 1	-	80.5	8.4	0.1	0.6	10.4	0.5
Sample 2	1.2	86.5	9.3	0.9	0.0	4.7	0.3

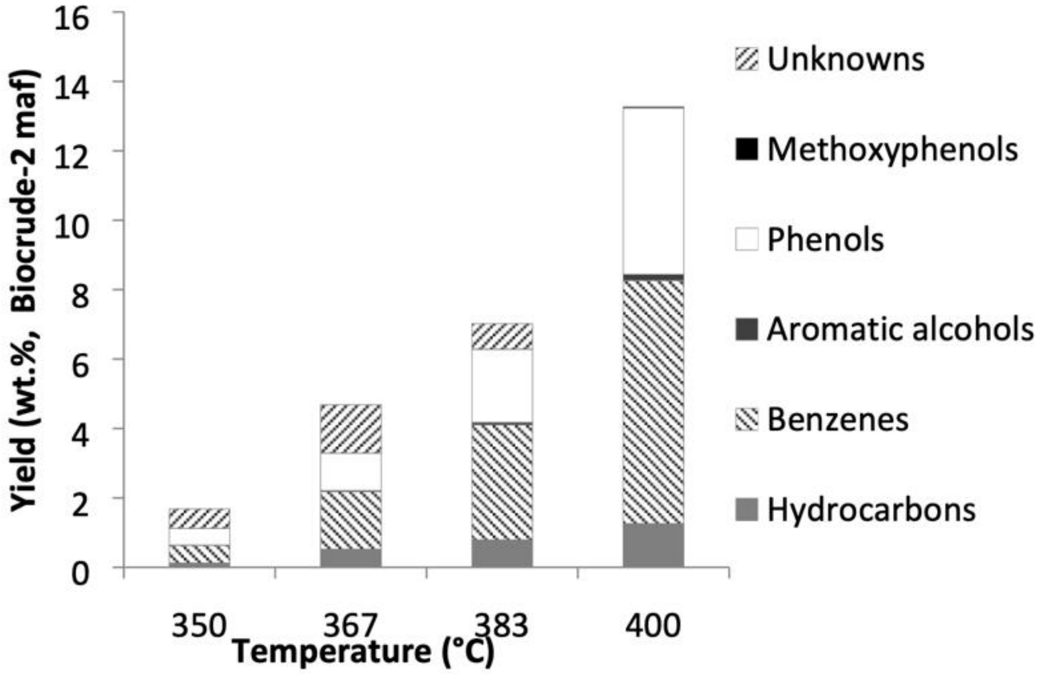
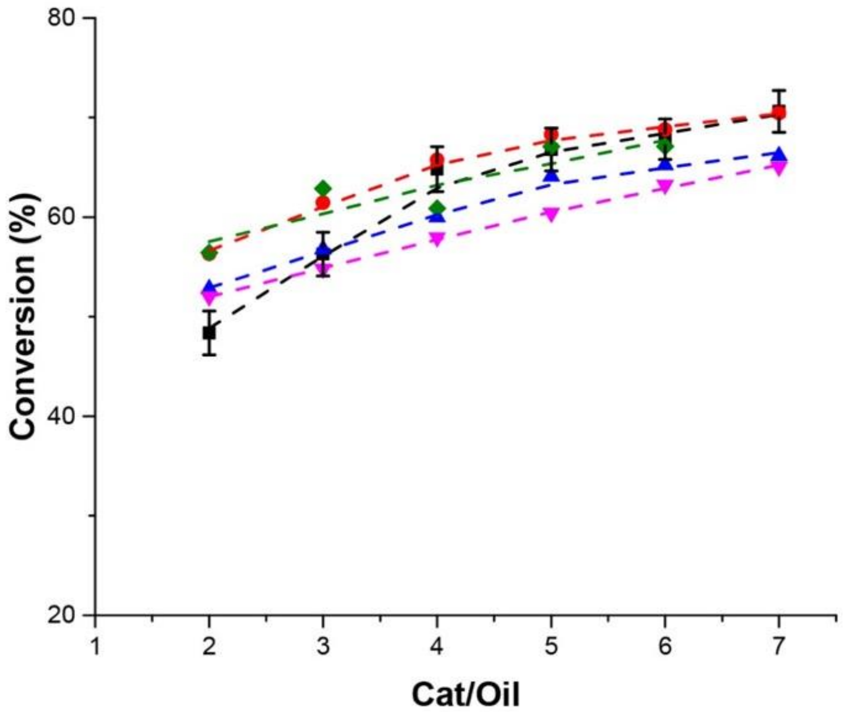


Figure 16. Quantities of monomers based on reactor temperature, separated into substance categories, Batch experiments (50 ml reactor) using 10 wt% catalyst, 6 hours, and 100 bar H2 pressure.

Figure 17 illustrates the catalytic cracking conversion rates as a function of the cat/oil ratio for pure VGO and VGO/HDO biocrude mixtures [8]. A slight increase in conversion was observed as the cat/oil ratio increased from 2 to 7 for all feeds. Lower conversions were found for HDO biocrude-2 compared to HDO biocrude-1, likely due to the presence of 9 wt% isopropanol, which falls within the boiling point range of light gases, even when unconverted. Notably, at higher cat/oil ratios, HDO biocrude-2 addition resulted in lower conversion compared to pure VGO.



ß

Figure 17. Conversion in MAT unit of 100% VGO (black), 82% VGO + 9% HDO biocrude-1 + 9% propanol (red), 90% VGO + 10% HDO biocrude-2 (blue), 70% VGO + 30% HDO biocrude-2 (pink), and 90% VGO + 10% propanol (green) as a function of the cat/oil ratio. Dashed lines represent locally weighted scatterplot smoothing (LOWESS) plots. The error bars are based on two repeated runs with pure VGO. [8]

4.3.2 Recent study upgrading duckweed via HDO

The study aimed to understand the product yields of upgraded oil, coke, gas, and WSP in the presence and absence of various catalysts [108]. The biocrude upgrading reactions were carried out at a temperature of 350 ± 2 °C and a pressure of approximately 18 MPa for a duration of 4 hours, with subsequent cooling by immersion in an ice water bath.

Effect of catalysts on the yields and

Regarding the influence of catalysts on upgraded biocrude yields, it was observed that the majority of catalysts led to a reduced production of upgraded biocrude during hydrothermal processing, particularly when set side by side against noncatalytic treatment outcomes [108]. Some reactions reflected mass balances that exceeded 100%, which could be postulated as being due to the incorporation of water or hydrogen into the product fractions [108]. Specifically, the zeolite-catalyzed reactions resulted in the most diminished oil yield at 64.7 wt.%, while the Co–Mo/γ-Al2O3-catalyzed reactions emerged as the most efficient, with a biocrude yield of 73.1 wt.%. It is likely that the distinct biochemical components inherent to feedstocks dictate reaction types and the biocrude yields during hydrothermal upgrading. As presented in Table 15, the mass balance closure for the reactions exhibited a range between 90.8 ± 4.7% and 104.7 ± 3.3%, contingent on the catalyst type utilized.

According to Zhang et al. (2014) it became evident that their formation during hydrothermal processing was primarily thermally driven [108]. In a noteworthy pattern, the gas yields resulting from catalyzed reactions were predominantly inferior compared to those observed from uncatalyzed reactions. Among the catalysts trialed, Ru/C and Rh/γ-Al2O3 demonstrated the most pronounced activity towards gas production. Regarding coke formation, all catalysts consistently demonstrated an enhancement in coke production relative to the non-catalyzed reactions. The zeolite catalyst took the lead in coke production, while the influence of metal presence was observed to potentially foster oil polymerization at elevated temperatures. The yields of water-Soluble Products (WSP) were consistent in the spectrum of different catalysts, with the singular exception being the notably elevated yield recorded with Pd/C. The WSPs predominantly consisted of compounds exhibiting high polarity.

Table 15. Effect of catalysts on the yields (wt.%) of different product fractions.

Catalyst type	Upgraded oil	Gas	Coke	WSP	Mass balance
No cat.	70.3 ± 3.5	14.3 ± 0.7	11.2 ± 0.6	6.0 ± 0.1	101.7 ± 4.9
Ru/C	67.6 ± 2.1	13.5 ± 0.6	17.5 ± 0.3	6.0 ± 0.3	104.7 ± 3.3
Pd/C	65.9 ± 1.1	5.8 ± 0.5	19.0 ± 2.1	8.0 ± 0.2	98.8 ± 3.9
Pt/C	66.7 ± 1.0	8.5 ± 0.5	17.6 ± 0.8	5.9 ± 0.1	98.7 ± 2.4
Pt/γ-Al_2O_3	64.8 ± 3.2	8.9 ± 0.4	15.8 ± 0.8	5.8 ± 0.2	95.2 ± 4.6
Pt/C, sulfide	68.1 ± 1.5	5.3 ± 1.2	18.7 ± 0.7	5.6 ± 0.1	97.8 ± 3.5
Rh/γ-Al_2O_3	67.7 ± 3.3	12.9 ± 0.6	13.4 ± 0.7	5.8 ± 0.2	99.9 ± 4.8
Activated carbon	66.5 ± 3.3	5.4 ± 0.3	12.9 ± 0.6	6.0 ± 0.3	90.8 ± 4.7
MoS_2	67.2 ± 3.3	4.8 ± 0.2	16.9 ± 0.8	5.7 ± 0.3	94.6 ± 4.6
Mo_2C	71.3 ± 3.5	4.8 ± 0.2	16.8 ± 0.8	6.0 ± 0.2	98.9 ± 4.7
Co–Mo/γ-Al_2O_3	73.1 ± 0.7	9.2 ± 1.4	17.3 ± 2.6	5.0 ± 0.2	104.6 ± 4.9
Zeolite	64.7 ± 3.2	9.5 ± 0.5	19.8 ± 1.0	5.4 ± 0.1	99.3 ± 4.8

Effect of catalysts on the properties of upgraded oil
According to Zhang et al. (2014) hydrothermal liquefaction (HTL) of duckweed upgrading resulted in biocrude with increased carbon (C) and hydrogen (H) contents and decreased oxygen (O) content. This altered elemental composition led to a higher energy density in the biocrude compared to the original duckweed feedstock (Table 16) [108].

Table 16. Moisture, ash, and elemental composition (wt.%, daf.) of duckweed, biocrude and upgraded oils (UPO) produced with different catalyst. [108]

	H_2O	Ash	C	H	N	S	O[a]	H/C	N/C	HHV (MJ/kg)	ER (%)
Duckweed	14.0	26.0	50.5	7.2	3.5	1.02	37.8	1.70	0.059	21.7	
Biocrude	1.0	0.8	73.4	7.9	4.7	0.38	13.6	1.30	0.055	33.5	0.20
UPO-No cat.	0.7	1.2	82.3	7.3	6.8	0.29	3.3	1.07	0.071	36.9	0.70
UPO-Ru/C	0.9	1.0	83.6	11.5	4.5	0.13	0.3	1.65	0.046	42.6	1.05
UPO-Pd/C	1.0	0.7	82.5	11.0	5.6	0.15	0.8	1.60	0.058	41.6	0.99
UPO-Pt/C	1.1	0.9	83.5	10.8	5.4	0.17	0.1	1.55	0.055	41.8	0.98
UPO-Pt/γ-Al_2O_3	1.2	1.1	83.6	10.3	4.8	0.17	1.1	1.48	0.049	41.1	0.91
UPO-Pt/C, sulfide	1.5	1.3	82.4	10.2	5.5	0.15	1.8	1.48	0.057	40.5	0.95
UPO-Rh/γ-Al_2O_3	1.2	1.1	83.0	9.8	5.3	0.17	1.7	1.42	0.055	40.3	0.90
UPO-Activated carbon	1.2	0.8	82.2	9.1	5.4	0.20	3.1	1.33	0.056	39.0	0.82
UPO-MoS_2	1.1	1.3	83.9	11.1	4.7	0.19	0.1	1.58	0.048	42.3	1.01
UPO-Mo_2C	1.7	0.7	83.5	9.3	5.6	0.22	1.4	1.34	0.058	39.9	0.91
UPO-Co–Mo/γ-Al_2O_3	1.3	0.7	80.2	8.3	5.9	0.17	5.4	1.24	0.063	37.1	0.84
UPO-Zeolite	1.1	0.9	83.7	9.9	5.0	0.18	1.2	1.42	0.051	40.7	0.89

Post-extraction, upgraded oils retained a certain level of moisture, ranging between 0.7 wt.% for uncatalyzed reactions to 1.7 wt.% for those catalyzed by Mo2C [108]. Both the biocrude and the upgraded oils showed approximately 1 wt.% ash content, possibly due to inorganic salt residues from the duckweed biomass. When different catalysts were introduced during the upgrading process, there was a decrease in O content and an increase in N content in the upgraded oil [108]. Most catalysts increased the C and H content of the upgraded oils. Ru/C demonstrated efficient sulfur removal and hydrogenation capabilities for the biocrude. Additionally, Pt/C produced upgraded oil with the lowest O content of all the catalysts tested.

In terms of energy conservation, the initial HTL process retained 27.8% of the chemical energy from the duckweed biomass in the biocrude [108]. The subsequent upgrading stages, when various catalysts were used, resulted in energy retention rates between 77.0% and 85.5%. Notably, the Ru/C-catalyzed reaction yielded the highest energy recovery rate of 85.5%. The inclusion of catalysts in the hydrothermal process improved energy recovery, with rates increasing from 77.0% without catalysts to over 80% with most catalysts.

4.3.3 Optimization Strategies for Biofuel Production: Interplay of Feedstock, Catalysts, and Process Condition

Optimizing the hydrothermal liquefaction (HTL) and hydrodeoxygenation (HDO) processes for biomass conversion into biofuel is essential for achieving sustainable energy sources. Factors such as the choice and consistency of feedstock, the catalyst/biocrude relation, optimal temperature, pressure values, and reaction time play pivotal roles in influencing the outcome of these processes. The HTL, focuses on depolymerizing lignin and limiting the oxygen content of the black liquor [8]. This emphasis on oxygen removal has been identified as a key marker for efficient co-processing [108]. If the oxygen content remains at higher levels after HTL, for example in the 23-29 wt% range [8], the subsequent need for HDO for further deoxygenation becomes apparent.

Feedstock
The type and variability of biomass feedstock significantly impacts the HTL and HDO processes. Biomass feedstock can range from lignocellulosic materials like wood and agricultural residues to algae and organic waste. The composition, moisture content, ash, and mineral content of the chosen feedstock can influence both the quality and yield of the biocrude. Inconsistencies in feedstock could lead to fluctuations in the biocrudes quality.

Pre-treatment
Pre-processing can involve an acid wash of HTL biocrude [8]. This process aids in mitigating the sodium salts and minimizing ash content [8]. Given the potentially adverse implications of sodium on the HDO phase and its capacity to deactivate catalysts like FCC Y-zeolite during coprocessing [8], the sample washing before HDO depending on the salt content can be crucial.

Catalyst and amounts
The catalyst-to-biocrude ratio is crucial in determining the yield and composition of the resulting product. According to Melin et al., (2022) (Figure 17), the higher relation yielded higher amount of biocrude. Studies on duckweed-based HTL biocrude upgrading show that various catalysts, including Ru/C and Rh/γ-Al_2O_3, demonstrated pronounced activity toward gas production, while the Co–Mo/γ-Al_2O_3-catalyzed reactions boasted the highest oil yield (at 73.1 wt.%) [108]. These findings emphasize the need to optimize the amount of catalyst to ensure efficient reactions.

Process conditions
According to the literature, temperature has a dual-edged effect on the process. While increased temperatures can lead to increased coking and strain of the equipment, it can also potentially increase the desired components in the yield [109]. Alternatively, lower temperatures may reduce costs, but may result in non-reactive or incomplete reactions and lower biocrude quality. [109]. Castello et al. (2019) conducted catalytic hydrotreatment of biocrudes from different feedstocks using a commercial NiMo/Al_2O_3 catalyst at different temperatures and pressures [74]. They observed that higher temperatures and pressures resulted in increased deoxygenation and improved fuel properties of the biocrudes. It was found that at higher temperatures and pressures, the oxygen content in the biocrudes decreased, resulting in higher heating values (HHVs) and improved fuel quality [74]. Certain specific temperature values could maximize benefits while minimizing negatives.
Pressure also plays a key role. High pressure, especially with hydrogen, can increase the yield of desirable components, especially as H_2 plays a key role in the deoxygenation of biocrude. Yet, if the pressure is too high, equipment might not withstand it, leading to operational challenges. Melin et al. (2022) illustrated the HTL of kraft black liquor under specific pressure conditions, emphasizing the importance of optimizing this parameter to improve biocrude quality [8].
Reaction time could improve the yield and composition of the biocrude but could also be associated with increased costs or risks such as excess coke formation. The properties of the upgraded oil, as demonstrated by research on black liquor-based HTL oil in the HDO process, suggest that optimal reaction times and specific temperature and pressure conditions are key in the refining process [8]. Excessive prolongation can be needles or even harmful.

In conclusion, achieving the ideal conditions for improving certain biomass and choosing specifically for that particular feedstock the most suitable catalyst requires a deep understanding of multiple interconnected factors.

5 Materials

This chapter provides an overview of the tools and techniques central to the research. The materials section outlines the materials, devices and chemicals used, providing a comprehensive inspection of the fundamental elements of the experiments.

5.1 Apparatus

5.1.1 Precision Weighing Instruments

The accurate and precise determination of sample masses was foundational to the experiments conducted in this study. To this end, a series of high-precision scales were employed, namely the Precisa XT 4200 C, Precisa 3000 CD, and Precisa 80 A-200 M (Figure 18).

Figure 18. A Comparative Display of the Precisa XT 4200 C, Precisa 3000 CD, and Precisa 80 A-200 M Scales in Action.

5.1.2 Ultrasonic bath

For the purpose of speeding up the mixing and dissolving of biocrude and solvent, an ultrasonic bath was employed. The model used was the S 180 H Elmasonic provided by Elma. This ultrasonic cleaner operates on 37 kHz. The unit is equipped with a stainless-steel tank and provides uniform distribution of ultrasonic waves, ensuring consistent and efficient processing of samples (Figure 19).

Figure 19. Ultrasonic bath.

5.1.3 Magnetic Stirring System

For thorough mixing and homogenization of solutions, a magnetic stirrer device was employed after using the ultrasonic bath to continue the dissolving of biocrude and isopropanol (IPA). The model utilized for the purpose of this study was the DREHZAHL magnetic stirrer by Heidolph (Figure 20). The device ensures a uniform and consistent stirring action. The stirring mode could be left on overnight under the fume hood, and for this, approximately 500 revolutions per minute (rpm) was used.

The magnetic stirrer was set up as follows:

1. The apparatus was placed on a stable, level surface to ensure consistent stirring performance.
2. The magnetic stir bar was placed into the vessel containing the solution to be stirred.
3. The vessel was then positioned on the stirrer's platform, ensuring proper alignment.
4. The desired stirring speed was set using the DREHZAHL's control mechanism to 400-600 and the device was switched on.
5. Upon completion, the device was turned off, and the stir bar was retrieved using an external magnet or by decanting the solution.

Figure 20. DREHZAL magnetic stirrer from Heidolph.

5.1.4 Rotavapor Evaporation System

For solvent evaporation and concentration purposes, the Rotavapor R-3 system from BUCHI was utilized. The R-3 model is designed for efficient and gentle removal of solvents from samples, benefiting from a precisely controlled evaporation process.

The Rotavapor R-3 was coupled with the BUCHI Vacuum System B-178, which aids in achieving the necessary vacuum conditions for solvent evaporation (Figure 21). The integrated vacuum controller B-720 ensures optimal control of the vacuum, allowing for adjustments based on the solvent properties and the desired evaporation rate.

Operational steps were as follows:

1. The sample was placed in the evaporation flask of the Rotavapor.
2. The flask was attached to the system, ensuring a proper seal.
3. The desired bath temperature and rotation speed were set on the Rotavapor R-3 (50 °C).
4. The BUCHI Vacuum System B-178 was activated, and the vacuum level was adjusted using the B-720 vacuum controller to achieve the desired evaporation conditions.
5. Once the evaporation was complete, the system was returned to atmospheric pressure, and the concentrated sample was carefully removed.

Figure 21. Rotavapor Evaporatory system.

5.1.5 The HDO batch reactor

The batch reactor designed by VTT is tailor-made for high-pressure reactions such as HDO biocrude reactions. Unlike continuous reactors, which continuously handle feed and effluent, batch reactors focus on a single batch of reactant and monitor its chemical reaction. This singular focus gives the batch reactor a unique adaptability that makes it perfect for laboratory-scale operations. This makes it an essential tool for refining and optimizing reaction conditions. The various parts of the HDO reactor system are represented and illustrated in the Figure 22.

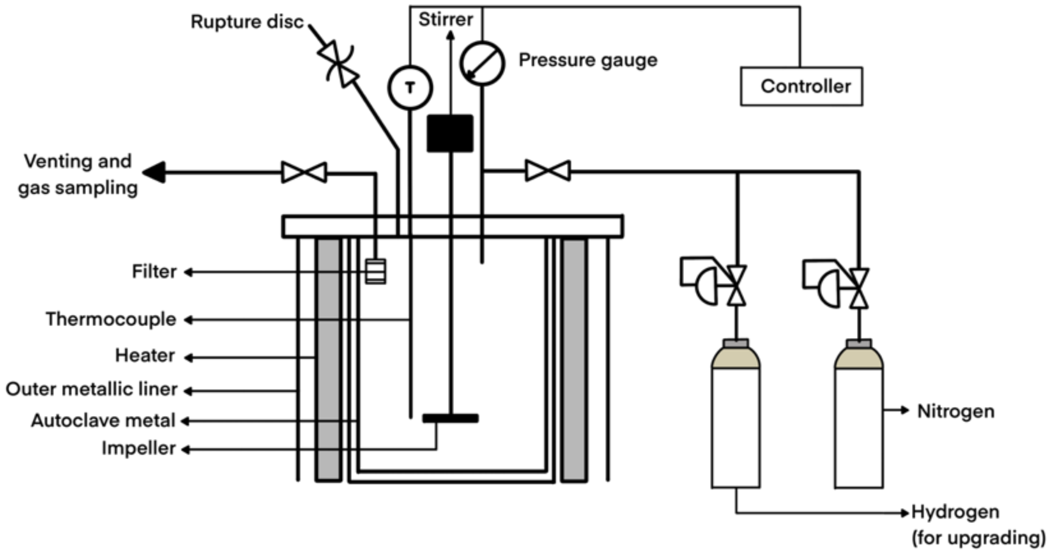


Figure 22. Schematic presentation of the used batch reactor (modified from a source [110]).

The VTT-designed reactor has a decent pressure handling capacity, allowing it to operate efficiently up to 245 bars. The safety valve used in the reaction was stated to withstand up to 270 bars, but it was noticed at preliminary tests, that the valve broke around 255 bars. This was one of the primary determining factors for the reactor conditions and was used to evaluate the maximum total pressure the reactor could withstand. The set temperature and initial hydrogen load in the beginning of the reactor were also calculated in order to stay below the crucial total pressure point.

For gas management, the reactor has a manual gas bottle feed system with a lever to control the amount of gas. Hydrogen is the primary reactant. Nitrogen provides the initial air removal and final safety. After each test, the reactor is purged with nitrogen to remove any harmful residual gases, ensuring a safe environment when opened. The reactor is equipped with an external valve designed for collecting gaseous samples. The heater is essential to the reactor and is automatically controlled by an external device to ensure precise temperature during the experiment. The analysis is collected using a computer connected to an analyzer that records the temperature and pressure inside the reactor. The stirrer that mixes the reaction works with a magnet attached to a motor by a leather strap (Figure 23). The mixing speed is controlled and adjusted outside the reactor room. The reactor has a water cooling system to maintain the temperature of the magnetic stirrer and prevent it from overheating. In addition, the reactor uses an air gun aimed at the heater to ensure rapid temperature reduction when required. The key components of the reaction control and monitoring systems are shown in Figure 24.

Figure 23. Outer look of the batch reactor, including the lid, water cooling, magnetic stir, and temperature- and pressure sensors.

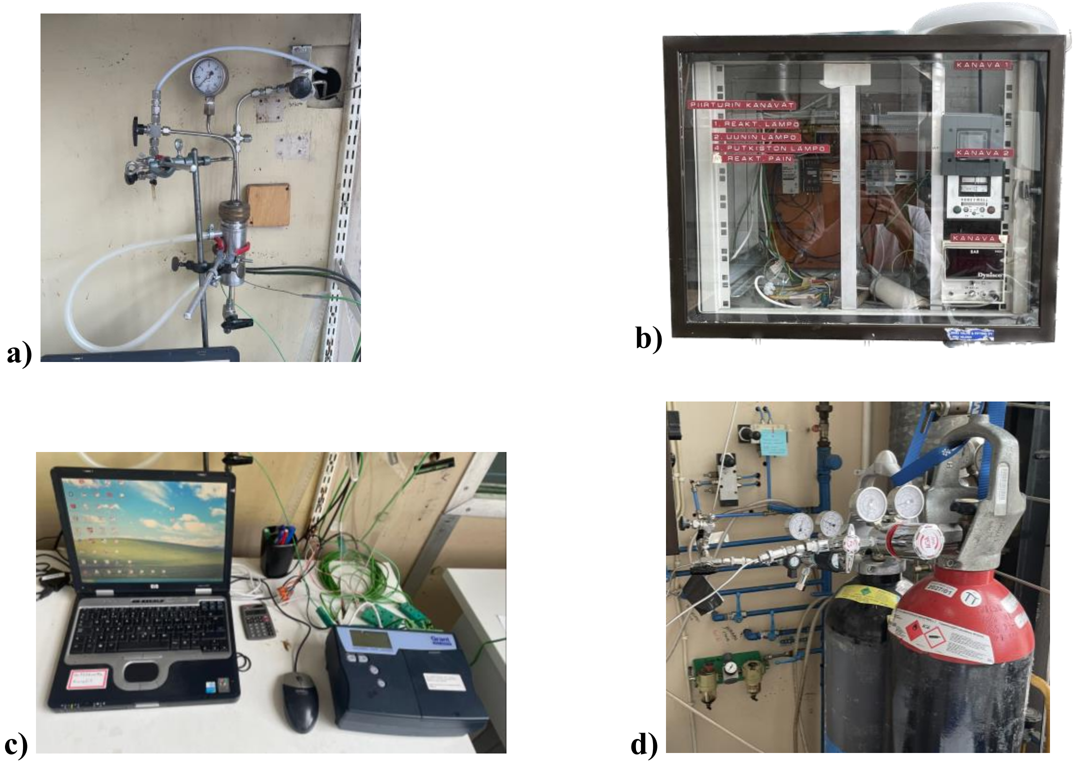


Figure 24. In the figures presented, the main operating pieces of the reactor system are depicted as follows. a) The external gas valve, b) the temperature controller, c) the computer displaying reaction condition values (including temperature, pressure, and time), d) The gas tanks accompanied by the magnetic stir controller.

5.2 Components and reactants

This chapter examines the critical components in catalytic conversion processes: Pine biocrude as the feedstock, the catalysts facilitating HDO reaction, and the chemicals involved in optimizing these processes.

5.2.1 HTL biocrude

The HTL biocrude sample provided by Aarhus University was an old sample from the pine biomass-based crude, and had a viscous if not solid essence, difficult to handle. Pine biocrude is a complex mixture containing a wide range of organic compounds and impurities, and its quality and composition can vary significantly based on the specific production process and conditions [111-113]. The oxygen content of pine crude bio-oil has been reported to vary widely, ranging from 11.3 wt% [114] to 40-45% [115].

The original HTL biocrude was tested in the beginning of experiments without pre-treating the sample at first to see how it performed in the HDO reaction. Due to difficult processing of the original sample (Figure 25), the sample was modified via pre-treating, to provide better yield for more true and precise results. In the following chapters the pre-treating process of the original sample is presented.

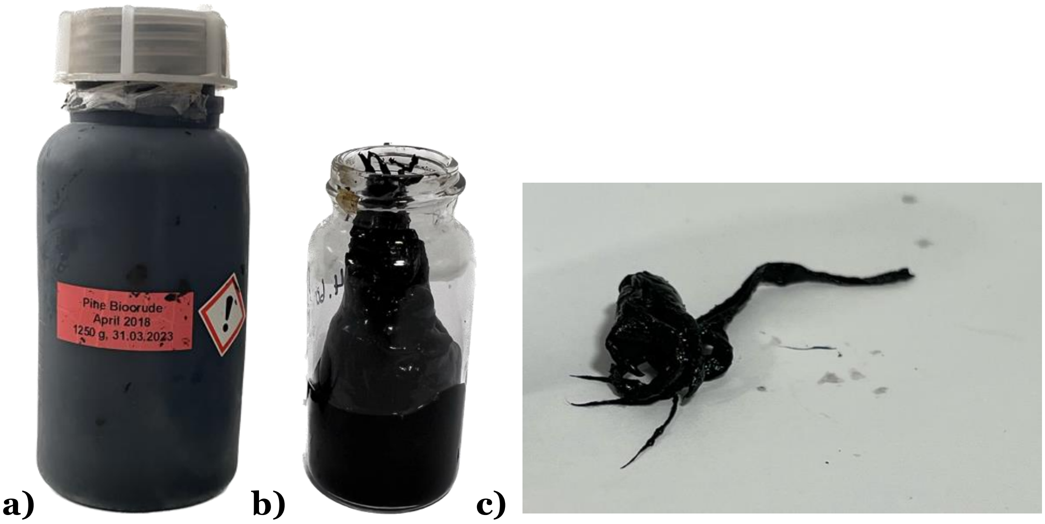


Figure 25. The original Pine biocrude sample. a) Presents the original package of the biocrude, b) shows the sample in a glass vial, and c) shows the sticky sample from up close.

5.2.2 Catalysts

Ruthenium-activated carbon and Nickel Molybdenum (BLF-07a) catalysts were used in this experiment, and both were sourced from Ranido. The ruthenium-activated carbon catalyst primarily comprises activated carbon, enriched with 5% of ruthenium. Ruthenium is a transition metal that is spread out over the large surface of the carbon, being the active metal of the catalyst. The Nickel Molybdenum catalyst, also from Ranido, typically possesses Molybdenum as the predominant active phase, with Nickel acting as a promoter. The ruthenium catalyst was the main catalyst for the tests (Figure 26).

Ruthenium catalysts have been reported to be more active and stable than nickel catalysts, making them an attractive alternative [116]. According to Yan et al. (2009), ruthenium is the most active catalyst for the hydrogenation of aliphatic carbonyl compounds [117]. The specific composition of the provided pine biocrude is not detailed but given the presumed higher lignin content due to its source, it is likely to contain a predominance of cyclic compounds over carbonyls. In line with this, ruthenium complexes have been used in the selective transformation of biomass-derived platform compounds, in particular lactones and cyclic acids [118]. Given these precedents, it's plausible to conclude that ruthenium activated carbon catalysts could be effective in catalyzing the transformation of saturated cyclic compounds typically found in biomass-derived biocrudes, such as the pine-based grade. Further chapters will elucidate their specific roles and possible effects in the experiments.

a) **b)**

Figure 26. Ruthenium activated carbon (Ru/AC). a) The original container of Ru/AC catalyst, and b) The Ru/AC catalyst in its sulfided form.

5.2.3 Chemicals

The following chemicals were used in conducting the experiments [119]. The specific use of each chemical is elaborated upon in the methods section. The used chemicals and their specific uses are presented and described below in Table 17.

Table 17. Chemical list used in the experiments.

Chemical Name	**Chemical Formula**	**Specific use**
Acetone	C_3H_6O	Primarily used as a solvent in cleaning processes.
2-Isopropanol	C_3H_8O	Used as a dissolver for original pine biocrude.
Ethyl Acetate	$C_4H_8O_2$	Acts as a dissolver for upgraded biocrude.
Dimethyl Sulfate	$(CH_3)_2SO_4$	Activation of hydrodesulfurization catalyst.
6-Hexane	C_6H_{14}	Utilized as a liquid medium to maintain the sulfided state of catalysts.

6 Methods

This methods section provides exploration of the principles of the experimental part of the thesis. The chapter discusses the methods needed to conduct the performed tests and analysis. The manner in which each material and device was used is detailed, followed by an overview of the analytical approaches, explaining the underlying motives and specific procedures behind each method. The chapter concludes with step-by-step descriptions of the testing processes, aiming to ensure a complete understanding of the research approach.

A series of experiments were performed with another HTL oil before receiving and starting the experimental part for better understanding of the reactor. This was done to ensure proper use of equipment and minimize errors in the actual study.

6.1 Catalyst qualification

The efficiency of three catalysts in the bio-oil upgrading process was evaluated under experimental conditions. The chosen catalysts were subjected to a uniform upgrading protocol to ensure the comparability of the results, with primary attention given to the yield, elemental composition, and deoxygenation of the upgraded biocrude. Each experiment was performed while maintaining constant reaction conditions across all catalysts to ensure fair comparison. These conditions included a hydrogen pressure of 30 bars, an operational temperature of 350°C, and an initial test duration of 4 hours. These primary trials were instrumental in assessing the performance of each catalyst under similar operational parameters.

The yield of upgraded biocrude was determined for each catalyst. The differences in yields were indicative of the catalysts' varying efficiency in converting bio-oil into a more refined and usable form of biocrude. In addition, an elemental analysis, and along with other analysis the deoxygenation of the upgraded biocrude was carried out. The elemental composition, primarily encompassing carbon, hydrogen, nitrogen, sulfur, and oxygen content, offered insights into the bio-crude's quality and the catalysts' effectiveness. By looking at the change in oxygen content, deoxygenation was measured to analyze the quality of the oil.

This assessment aimed to offer insights for the selection of optimal catalysts for the upgrading process. However, it is important to note that the experiments with the goal to find the most ideal HDO conditions had started with sulfided Ruthenium activated carbon (Ru/AC) catalyst prior to obtaining the results from comparative experiment.

6.2 Experimental design and HDO setup

The primary objective of this study was to optimize the HDO conditions to enhance the catalytic performance while ensuring the stability of the catalysts. To achieve this, a 2-level Design of Experiments (DOE) approach was employed, considering three independent variables: temperature, pressure, and time. Additionally, two middle value tests were performed to further explore the effects of the central points on the HDO process and to validate the repeatability. More tests and repetitions would have been an ideal addition to the test, but as the test were time consuming, the number of tests needed to be eliminated.

6.2.1 Design of Experiments (DOE)

The DOE approach is a powerful and efficient method for systematically evaluating the influence of multiple variables on a process. It allows for the identification of significant factors and interactions, enabling the determination of the optimal process conditions.

Experimental Runs

A total of 14 experimental runs were performed in a randomized order to minimize bias and account for any potential sources of variability. Each experimental run represented a specific combination of temperature, pressure, and time based on the selected levels for the independent variables and the central points. The limiting factor in setting the reactor conditions was the end limit of total pressure that the reactor and the pressure valve allowed. To this both temperature during the reactor and the loaded hydrogen would affect together. Therefore, both reactor temperature and initial hydrogen load had to be considered carefully together when determining their dual effect. The effect of load of hydrogen would be linear to trend, but the trend for water pressure in correlation to water temperature would be nonlinear. The following tests were concluded so that the pressure valve limit (255 bar) would not be exceeded, as described in the chapter 6.4.2 (HDO batch reactor).

The temperature was selected as one of the primary independent variables, with two levels defined: 320°C as the minimum value and 380°C as the maximum value. These values were chosen based on prior literature and preliminary experiments, aiming to explore the impact of varying HDO process temperatures on the materials and to reach supercritical conditions for water. Pressure was another crucial independent variable in the sulfidation process. Two levels were considered: 5 bars as the minimum value and 15 bars as the maximum value. The selected pressure range aimed to assess its influence on the sulfidation extent and catalyst performance. Time, representing the duration of the sulfidation process, was the third independent variable. The two levels were set at 2 hours (minimum) and 4 hours (maximum). The chosen range was based on preliminary studies and was expected to provide insights into the reaction kinetics and the effect of prolonged exposure to sulfidation conditions.

To investigate the influence of the central points on the HDO process conditions, two middle value tests were performed at intermediate levels for the independent variables. The central points were included to evaluate potential non-linear effects or interactions between the variables and to ensure a robust analysis of the experimental results. The points and the experimental design represented below as a 3D-image Figure 27.

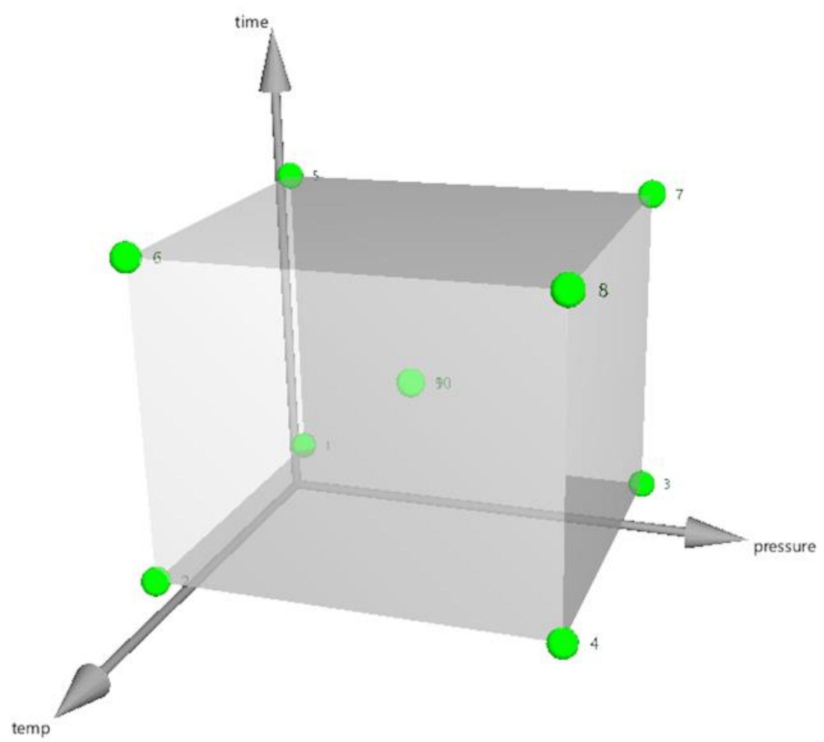


Figure 27. 3D-image representing the experimental setting such as the number of tests.

Data Collection and Analysis
During each experimental run, relevant parameters such reaction conditions were overseen and recorded, and the biocrude data analyzed in terms yield and elemental composition to calculate the deoxygenation. The obtained data was implemented to the statistical software (MODDE) and analyzed to

identify significant factors and potential interactions between the conditional variables to yield and deoxygenation. The results of the DOE analysis were used to investigate the effects of temperature, pressure, and time of the process for the catalysts.

6.3 Preparation of catalysts and reactor set up

This chapter provides insight on how the reactor was operated and maintained, and how the set-up of the reactor was performed. The sulfidation of the catalyst were the initial steps in the experiments. Similar operational steps are done in the following HDO tests. Therefore, this chapter focuses also to give more detailed steps, and clarify the set-up of HDO reactor.

6.3.1 Reactor set up and catalyst sulfidation

The batch reactor with a volume capacity of 1000 mL, the same which would be used in HDO experiment was used in the sulfidation process. The reactor was equipped with a magnetic stirrer to ensure proper mixing of the reactants during the sulfidation process. A pressure gauge and a safety relief valve were installed to monitor and control the pressure within the reactor, ensuring safe operation throughout the experiment. The reactor was thoroughly cleaned and purged with nitrogen gas before use to eliminate any traces of oxygen and moisture that could affect the sulfidation reaction.

The catalysts used in this study were obtained from Ranido in an unsulfided form. These catalysts were selected after discussion with project partners Ranido and PSI, based on their composition and activity towards the desired chemical reactions, and to fit the required conditions. Sulfidation is a process that involves infusing a material, often a catalyst, with sulfur [120].This process is commonly used to enhance the activity and stability of catalysts. For example, in the study by Wang et al. (2014), they performed a sulfidation treatment on spent sulfide catalysts to supplement sulfur and recover their activity [121]. This indicates that sulfidation can improve the performance of catalysts.

6.3.2 Sulfidation Conditions

The sulfidation process was carried out using the batch reactor and loading it with hydrogen (H_2). Hydrogen was chosen due to its reactivity with sulfur species, facilitating the formation of active sulfide phases on the catalyst surface. Moreover, dimethyl disulfide (DMDS) was utilized in conjunction with hydrogen to add a sulfur source in the catalyst's sulfidation. The catalyst was initially mixed with DMDS and hexane before being subjected to the sulfidation conditions. The use of DMDS and hexane aimed to enable a more uniform and extensive sulfidation throughout the catalyst. The sulfidation conditions were optimized based on preliminary experiments performed by VTT and Ranido to achieve the desired sulfidation extent and avoid potential catalyst deactivation. The sulfidation process was conducted at a constant temperature of 325 degrees Celsius and under a pressure of 30 bars of hydrogen gas. The elevated pressure favors the interaction between hydrogen and sulfur species but also promotes the penetration of sulfur species into the catalyst's porous structure, maximizing the sulfidation extent and enhancing the catalytic activity. The 4-hour duration was determined to be sufficient for the completion of the sulfidation reaction, leading to the formation of the desired sulfide species on the catalyst surface. During this period, the catalysts initially sulfurized and mixed with DMDS and hexane. These conditions were also selected to ensure a balance between sulfidation efficiency and catalyst stability.

6.3.3 Catalyst Sulfidation Procedure

The sulfidation procedure followed a step-by-step approach to ensure precise and reproducible experiment:

1. The batch reactor was thoroughly cleaned using deionized water and acetone and left to dry after each reactor run.
2. The unsulfurized catalyst (20 g) was loaded into the autoclave with the hexane (around 100 ml) and DMDS (7 ml).
3. The reactor was sealed, and the reactor was purged with nitrogen around 5 times. The reactor was tested for possible leakage, at 60 bars of nitrogen. Hydrogen (H_2) gas was introduced and washed 3 times with 10-20 bars of H_2 pressure and then left to desired pressure of 30 bar.
4. The reactor's magnetic stirrer was activated (2000 rpm) to ensure proper mixing of the catalyst during the sulfidation process.
5. The reactor was heated to the sulfidation temperature of 325 degrees of Celsius and held at this temperature for 4 hours.
6. After the sulfidation period, the reactor was allowed to cool down to a room temperature using a cooling air pistol.
7. The reactor was washed using nitrogen to cleanse from harmful toxins from the reactor before opening the reactor.
8. The sulfided catalyst were then carefully removed along with remaining liquids from the reactor and stored in a container to prevent exposure to air or moisture.

6.4 Pine biocrude upgrading and treatment

6.4.1 Biocrude pre-treatment

During the initial stages of experimentation, the biocrude was tested in its untreated form. As a results of this test, challenges arose when attempting to introduce the sample into the autoclave to ensure proper mixing, and later when attempting to recover and separate the oil after the reaction. These obstacles prompted modifications in subsequent experiments. Given these challenges, the focus of subsequent trials was on the pre-treatment and after-treatment of the biocrude samples. To enhance the yield recovery, the protocol was modified to include post- and after reaction treatment for biocrude. The materials section emphasized the significantly high viscosity of the biocrude, requiring specific preparation techniques to render it adequate for reactor conditions. Without preparatory and post-treatment processes, the biocrude's solid wax like consistency would disturb its flow and hinder its efficient mixing and interaction within the reactor, even under the most adverse conditions. Extracting the sample from the autoclave or isolating the oil from the solid remnants in necessary quantities would be impractical for this type of pine-derived biocrude.

The samples were pre-treated by dissolving it first to 2-isopropanol (IPA), filtering the solids using suction filter, and then by evaporating the IPA. Ethyl acetate was used in the matter of dissolving the biocrude after the reaction experiment and performed very similarly as IPA. The procedure of dissolving biocrude in isopropanol or ethyl acetate dissolve certain components and reduces its viscosity, allowing for filtration without altering the structure of the biocrude itself. The use of solvents such as ethyl acetate, methyl isobutyl ketone, methanol, acetone and ethanol has been investigated to reduce and stabilize the viscosity of pyrolysis oils similar to biocrude [122]. In addition, the use of co-solvents such as ethanol, isopropanol, ethylene glycol and glycerol has been investigated in hydrothermal liquefaction to understand their impact on the treatment of biomass such as microalgae [123], and the use ethyl acetate in increased extraction of biocrude with higher energy recovery in HTL upgrading [124]. A VTT partner PSI also recommended IPA for dissolving the biocrude. Choosing the same solvent seemed natural as it worked.

The dissolution of the pine biocrude was carried out in a 350 ml glass container using approximately 100 g of biocrude and 200 ml of solvent in a 1:2 ratio. The mixture was placed in an ultrasonic bath for at a minimum of 45 minutes to facilitate dissolution and then stirred with a spoon to accelerate the process. Once the pine biocrude showed the desired flexibility, a magnetic stirrer was placed in the mixture. Magnetic stirring was continued overnight to ensure complete homogenization of the solution.

Filtration was then carried out to remove solids from the mixture to facilitate handling and subsequent processing of the biocrude. Suction filtration was used to remove reaction inhibiting solids and to reduce the viscosity of the biocrude to improve its miscibility with the catalyst. The filtered biocrude in isopropyl alcohol (IPA) solution was transferred directly to a heat resistant flask which was then used to evaporate the solvent.

6.4.2 HDO batch reactor

The upgrading experiments were conducted in a 1000 mL autoclave reactor (Figure 22). For a typical run, approximately 28 g of biocrude, 2.8 g of catalyst, 128 mL of deionized water, and 0.15, 0.30, or 0.45 mol H_2 were loaded into the reactor, equating to about 5-15 bars of H_2. In the beginning, after closing the reactor with the complete set of catalyst, water and biocrude, and before starting the reaction, the reactor was flushed first with 60 bars of nitrogen around 5 times, and then with hydrogen with around 20 to 30 bars of hydrogen around 3 times. The high pressure load with nitrogen was also performed to reveal potential leakage due to an incomplete seal. To further ensure pseudo-homogeneous reactions, the reaction mixture was mixed using a magnetic stir bar. The upgrading was performed with three different temperatures and 3 different hydrogen pressure load values. The examined temperature values were 320 °C, 350 °C, and 380 °C, and hydrogen load for each temperature value were 5, 10, 15 bars. Both temperature and pressure were evaluated during the whole reaction via transferring data from heat and pressure sensors to an external computer recording the data in excel format.

The upgrading reactions were carried out by placing the autoclave into the reactor. The heating time naturally varied between the reactions with different temperature sets. Let us note that the recording of the reaction time would begin 5 degrees before the aimed temperature value. For the minimum temperature value of 320 °C, the duration of heating was 65 minutes. Medium temperature, 350 °C was reached in 80 minutes, and the highest, 380° was reached in 90 minutes. The cooling time of the reactor was inaccurately assessed. The cooling pistols' position had a great impact on the cooling time. However, to provide an overview, the cooling duration varied between 1 hour to 2,5 hours.

In the temperature ranges studied (320°C to 380°C), the internal pressure of the reactor varied significantly, initially between 110-232 bar. This pressure range suggests that the medium in the reactor was in a liquid state up to 220 bars, as the high pressure raised the boiling point of water well above standard conditions [125, 126]. Above 220 bar and at higher temperatures above the critical point of water (approximately 374°C), the contents of the reactor enter a supercritical state. In this state, conventional distinctions between the liquid and gas phases no longer apply, reflecting a unique phase in which water adopts properties intermediate between those of liquids and gases. Under these supercritical conditions, the solubility characteristics and reaction kinetics are significantly altered compared to those in standard liquid water or steam. This leads to increased solubility for different substances and potentially different reaction pathways, providing a novel medium for chemical reactions. The density of supercritical water, which is significantly higher than that of steam but lower than that of liquid water, combined with its enhanced diffusivity, which is closer to that of a gas, makes it an exceptionally effective solvent for certain chemical processes.

The temperature was maintained at the targeted temperature using a temperature controller. Upon reaching a reaction time of 2, 3, or 4 hours, the heater was turned off and an air pistol was directed at the reactor to cool it, thereby stopping the reaction. The cooling duration varied depending on the reaction temperature; for the 320 °C, 70 minutes were needed to cool the reactor to a safe handling temperature, for 350 °C, it took 80 minutes, and for 380 °C, approximately 90 minutes.

Without filtering the separated phases, the water phase was poured into a glass container. Notably, a small fraction of liquid oil would transfer with the water phase. In the autoclave, 100 mL of ethyl acetate was added to dissolve the upgraded oil fraction and was left overnight to dissolve using a magnetic stir. The outer part of the autoclave inside the reactor, was also treated with a small amount of ethyl acetate to aid In the retrieval of the sample.

The liquid ethyl acetate biocrude extracts were filtered using standard filter paper and transferred to a 250 mL flask for evaporation. The autoclave and reactor were washed with excess ethyl acetate, which was also transferred to the flask through filter paper. The filter paper and solid residue were left under a fume hood for 4-7 days to dry and were weighed to calculate non-catalyst solid residue.

The amount of coke, defined as non-catalyst solid residue, was calculated by subtracting the catalyst weight from the solid residue weight. The liquid ethyl acetate biocrude solution was then evaporated, leaving only the upgraded oil. The yield of each product fraction was calculated by dividing its mass by the mass of the product loaded using the Eq. (4) [127].

$$Yields_{oil,solid\ residue\ (coke)} = \frac{Weight\ of\ the\ product}{Weight\ of\ the\ biocrude} \times 100 \qquad (4)$$

6.4.3 After-treatment

After HDO, the process moved to after-treatment. The autoclave in the reactor consisted of water, biocrude and solids phases. The water phase on top could be separated by simply pouring it out of the autoclave without having to worry about the biocrude or solids falling out of the autoclave because they were either so viscous or stuck to the bottom like solid. This made it easy to remove the water, but very difficult to remove the biocrude and solids as they were solid like in viscosity and stuck to the bottom of the autoclave. Another problem was that the biocrude and solids were mixed together in the same phase. This also emphasized the need to use a solvent when removing the biocrude from the autoclave. It is important to note that a few drops of biocrude were transferred to the water phase during the experiments.
Ethyl acetate was measured into the autoclave at about 100 ml in excess compared to the remaining solids in the bottom. The autoclave was returned to the cooled reactor setup immediately after each reactor run and left overnight with mixing on. The next morning (15-18 hours later) the biocrude and solids had dissolved, and the solution could be filtered, and the phases completely separated.

6.4.4 Procedure overview

This section provides an overview of the hydrodeoxygenation (HDO) process, including both pre- and post-treatment steps. The pre- and after-treatment procedure is summarized below and presented in the Figure 28.

Pre-treatment:

1. Dissolve and separate the solids from the original pine biocrude (IPA).
2. Filter solids from the biocrude using a suction filter.
3. Evaporate the IPA.

HDO:

4. Pine biocrude HDO. Fill the reactor with biocrude (25 g), catalyst (2,5 g), and water (125 g). Perform the cleansing of the reactor with nitrogen and fill with hydrogen. Set the desired temperature and safety measures. (Chapter 6.3.1)

After treatment:

5. Separate the water phase by pouring the water phase into its own container and dissolve the remaining biocrude using ethyl acetate. Leave the solvent into reactor with mixing on overnight.
6. Filter the solids (undissolved coke + catalyst) form the biocrude solvent solution.
7. Evaporate the ethyl acetate from the upgraded biocrude.

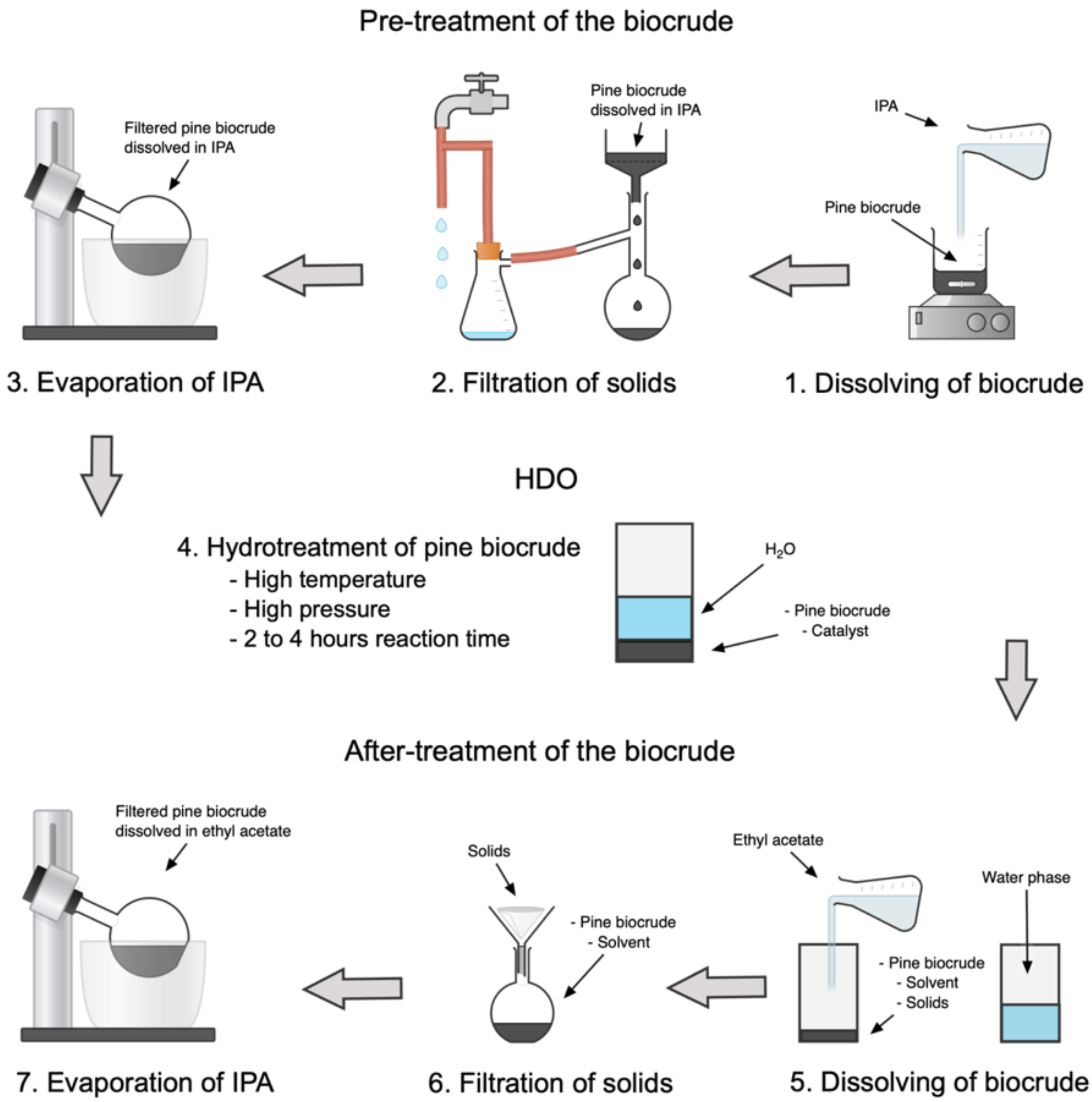


Figure 28. Description of the sample treatment before and after upgrading.

6.5 Analyses

The product from the reaction has different phases: gas, aqueous, oil, and solid phase. To thoroughly understand the properties of this upgraded biocrude oil, it is necessary to analyze its different phases, including the gas, aqueous, oil, and solid phases. Each phase requires a unique analysis approach to assess the composition of interest accurately, such as analyzing H_2, C, an N. In addition, while the solids consisted of used catalyst particles, other components are also essential to inspect.

The determination of the elemental composition of the biocrude was carried out in a manner that aligns with the method employed by Channiwala and Parikh (2002) [54]. This involved calculating the higher heating value (HHV) of the materials based on their specific elemental composition. The constituent elements considered in these calculations were carbon (C), hydrogen (H), sulfur (S), oxygen (O), nitrogen (N), and ash (A). Each of these constituents was measured as a mass percentage of the dry weight of the material.

This approach provided an accurate measure of the HHV of the biocrude, enabling a comprehensive assessment of their potential energy value [54]. These calculations were critical in comparing and evaluating the biocrude products, pre-treated biocrude batches, and the original pine biocrude based on their energy potential, facilitating further scientific inquiry and potential applications of these materials.

Key parameters enhancing biocrude:

- **H/C ratio**: Higher values can indicate a more saturated nature of the organic material [128]. A higher H/C ratio is generally seen as favorable for fuels as it can signify higher energy content and lower reactivity.
- **Deoxygenation**: Deoxygenation aims to remove oxygen from the biocrude to improve its quality and energy content, transforming it into a more stable and hydrocarbon-rich fuel comparable to conventional fossil fuels [114, 129].
- **HHV**: A higher HHV indicates a higher energy content in the fuel. Comparing the HHV of the original and upgraded bio-oils can give an indication of the effectiveness of the upgrading process (1)) [54].
- **ER**: Energy recovery (ER) in biocrude upgrading refers to the efficiency of energy recovery during the upgrading process [55]. It is a critical parameter that reflects the effectiveness of the upgrading process in improving the energy density and physical properties of the biocrude (2)).

Procedure for analyzing the phases:

1. For the gas phase, the gas was collected in a suitable gas-tight container and then analyzed using Gas Chromatography device.
2. For the aqueous phase, the sample was removed of any suspended solids, placed in a glass container, and sent to TOC, KF-titration, and sulfur analysis.
3. For the oil phase, after separation of solids and removing the solvent, the biocrude transported from a flask to glass bottles for CHN-, KF-titration, and sulfur analysis.
4. For the solids, the solid residue dried and into a fine powder consisting partly of the coke formed from the biocrude, and the remaining catalyst.

6.5.1 Analytical techniques and statistical tools in analysis

Elemental analysis (CHN)

CHN analysis is an essential technique for determining the percentage of carbon, hydrogen and nitrogen in samples [130]. It is essential for understanding the elemental composition of biomass fuels, such as biofuels derived from plants and animals, and helps to assess the viability, CO_2 emission levels and energy balance of these fuels.

This technique is based on the complete and total combustion of the sample in the presence of excess oxygen [131]. During this combustion, the carbon present in the sample is converted into carbon dioxide (CO_2), the hydrogen into water (H_2O) and the nitrogen into a combination of nitrogen gas (N_2) and other nitrogen compounds such as nitrogen oxides (NOx) [130, 131]. After combustion, the gases produced are separated and passed through specialised detection instruments, often gas chromatographs or mass spectrometers. By measuring the amounts of CO_2, H_2O and NOx or N_2, and using the known stoichiometry of the combustion reactions, the original percentages of carbon, hydrogen and nitrogen in the sample can be accurately calculated.

The CHN-analysis for the biocrude and solid coke samples were performed by VTT Bioruukki, Nea Palmunen.

Gas chromatography (GC-MS)

Gas chromatography (GC) is an analytical technique that separates and analyses compounds within complex mixtures, such as HTL biocrude and upgraded products which can include nitrogen-containing compounds, ketones, alcohols, and oxygenated aromatics [132-134]. The initial step involves the injection of a sample into the chromatograph, leading to its vaporization. An an inert gas, typically helium or nitrogen, propels the vaporized sample through a separation tube or column. Gas chromatography separates a sample's parts by how fast they pass through a column, based on their interaction with the column's material. A detector then measures these parts to identify the sample's composition. The precision of this method is notably enhanced by comparing the test sample against a reference sample with a known concentration. This comparison uses the retention time—the time components take to exit the column—and peak area as indicators for determining concentrations.

TOC

The Total Organic Carbon (TOC) instrument used in this study was installed in 2010 at the School of Chemical Engineering and measures total organic carbon (TOC) in water, adhering to standard SFS-ISO 8245 [135]. Utilizing analytically-aided combustion oxidation at 680°C and non-dispersive infrared detection (NDIR), it offers a measurement range of 0–25,000 mg/L for TC and 0–30,000 mg/L for TOC, with a detection limit of 4 µg/L for TC, TOC, and IC. The system allows for sample injection volumes ranging from 10 to

2,000 μL and in-syringe dilution factors from 2 to 50 times. These tests were performed by Tuyen Nguyen from Aalto University.

KF-titration
Karl Fischer (KF) titration is a specialized analytical technique used to accurately determine the water content of samples. Karl Fischer's method, developed in 1935, uses a Bunsen reaction to determine water content: sulfur dioxide reacts with iodine in the presence of water to form sulfuric acid and hydrogen iodide [136]. During titration, iodine solution is added to the sample until the water has fully reacted. Methanol assists this reaction, and a base neutralizes the acid formed. The end of the titration is marked by a stable iodine level, indicating that all the water has reacted. The iodine used correlates directly with the water content of the sample, allowing it to be quantified. The KF-titration was performed by VTT Bioruukki

Statistical analysis (Modde)
MODDE utilized Analysis of Variance (ANOVA) to scrutinize the significance of the various factors and their interactions within the experiment [137, 138]. The resulting ANOVA table summarizes the impact of each variable and their interplay on the experimental outcome. This analysis allows to discern which variables significantly influence the results.

6.5.2 The principle of mass- and carbon balance analysis
This chapter describes the principle of determining mass- and carbon balance and provides definitions for the used terms. The mass- and carbon balance values utilized the data from the elemental analysis (CHN), gas chromatography (GC-MS), Karl-Fisher titration (KF-titration), and sulfur content analysis. Based on these analysis methods, the mass- and carbon balances for upgraded biocrude, gas phase, water soluble products (WSP), and coke after the HDO reaction were calculated. The focus in calculations is understanding the mass and carbon transfer and transformation efficiency of the upgrading process from biocrude to upgraded biocrude, and the generation of gaseous products, WSP, and coke to the initial mass of biocrude (mass balance) or to the mass of carbon in biocrude (carbon balance) when assessing carbon movement. This perspective is particularly useful for assessing the efficiency and effectiveness of the upgrading process, such as HDO, in enhancing the quality of biocrude and quantifying by-product formation.

In the HDO process, certain components of the biocrude are converted into gaseous products which were studied from the gas phase using GC-MS. The gas phase after the HDO reaction, is typically a mixture of hydrogen, carbon monoxide, carbon dioxide, short-chain hydrocarbons and various other chemicals [74]. Water soluble organic and inorganic compounds from the biocrude result in an aqueous solution or water-soluble fraction (WSP) [139]. The mass balance in the aqueous solution focuses primarily on describing the preservation of water in the work, whereas the carbon balance focuses more on the carbon balance of WSP, in other words the percentual conversion of carbon from the initial biocrude to the water phase. The upgrading of biocrude also results in the formation of coke. The production of coke serves as a marker for the efficiency of the biocrude upgrading process. In general, higher coke formation indicates a less efficient conversion of biomass into liquid and gaseous fuels.

The **mass balances** were calculated as follows:

1. **Upgraded biocrude:** The mass balance of the upgraded biocrude values were calculated by comparing the initial mass of the biocrude measured at the reactor with the yield of the final upgraded biocrude. The principle for calculating mass balance for upgraded biocrude represented in equation (5).

$$Mass\ balance_{Upgraded\ biocrude}(Yield) == \frac{m_{Upgraded\ biocrude}}{m_{Initial\ biocrude}} \times 100\% \quad (5)$$

2. **Gas:** The mass balance of gas was calculated by first calculating the initial mass of gas at the beginning of the reactor, assuming that the free volume together with the reactants consisted of pure hydrogen. Then, after the reaction, the gas mass was calculated based on the GC tests. The initial mass was subtracted from the final mass of the gas in the reactor, and the changed mass was compared with the initial mass of the biocrude before the reactor to see how much of the biocrude was transferred to the gas phase. The principle for calculating mass balance for gaseous products (equation (6)).

$$Mass\ balance_{Gaseous\ products} = \frac{m_{Gas,\ after} - m_{Gas,\ begin}}{m_{Initial\ biocrude}} \times 100\% \quad (6)$$

3. **Aqueous solution:** Aqueous mass in the reactor was calculated by basically determining yield in water (equation (7)) because the water preservation was so low and fluctuating between tests, there was no point calculating the biocrude mass transfer to the water, because it would have given incompetent results. To address the problem, calculating the addressed the problem. In the carbon balance calculation, the transfer of carbon to the water was assessed with more accurate approach and results.

$$Mass\ balance_{Water}\ (Yield) = \frac{m_{water,\ after}}{m_{water,\ before}} \times 100\% \quad (7)$$

4. **Coke:** The mass balance of the coke (solids) was calculated by looking at the change in the mass of the solids and comparing this change with the mass of the biocrude, similar to the other phases. First, the weight of the solids at the beginning of the reactor, which consisted of the catalyst, was measured. At the end, the filtered solids were weighed and this change in solids (taking catalyst weight into consideration) was compared with the initial mass of biocrude before the HDO reaction (equation (8)).

$$Mass\ balance_{coke} = \frac{m_{coke,\ after} - m_{catalyst,\ begin}}{m_{Initial\ biocrude}} \times 100\% \tag{8}$$

The **carbon balances** were calculated as follows:

1. **Upgraded biocrude:** The amount of carbon in the biocrude sample was calculated from the CHN and KF titration analyses. The amount of carbon measured from the upgraded biocrude was calculated and compared to the carbon content of the used initial biocrude batch sample before reaction (equation (9)). This provided the initial and post reaction carbon yield in the oil phase.

$$Carbon\ balance_{Upgraded\ biocrude} = \frac{m(C)_{upgraded\ bio,\ after}}{m(C)_{Initial\ biocrude}} \times 100\% \tag{9}$$

2. **Gas:** The carbon content was calculated from the GC results by analysis of the components in the gas. The calculated mass of carbon change, more precisely the increase, was compared with the initial biocrude carbon mass and the percentage change in gas phase carbon relative to the initial biocrude was calculated (equation (10)).

$$Carbon\ balance_{Gaseous\ products} = \frac{m(C)_{Gas,\ after} - m(C)_{Gas,\ begin}}{m(C)_{Initial\ biocrude}} \times 100\% \tag{10}$$

3. **WSP:** The carbon balance of the WSP was calculated similarly to the gas carbon balance, but TOC analysis was used to determine the amount of carbon in the water. The amount of water at the end was used to calculate the total amount of carbon in the water. Finally, the total amount of carbon was compared to the carbon content of the initial biocrude to show the percentual amount of carbon from biocrude in the water (equation (11)).

$$Carbon\ balance_{WSP} = \frac{m(C)_{WSP}}{m(C)_{Initial\ biocrude}} \times 100\% \tag{11}$$

4. **Coke:** The carbon balance of the solids was calculated by taking into account the initial carbon content of the catalyst and calculating the final carbon content of the filtered solids. The solids were analyzed by CHN analysis. The total amount of carbon in the catalyst was subtracted from the total amount of carbon in the filtered solids, and the remaining amount was used to compare the carbon content in the coke between the carbon content of the biocrude (equation (12)). This would represent the formed percentual carbon from the initial biocrude.

$$Carbon\ balance_{Coke} = \frac{m(C)_{Coke,\ after} - m(C)_{catalyst,\ begin}}{m(C)_{Initial\ biocrude}} \times 100\% \tag{12}$$

7 Results and Discussion

This chapter aims to present the results and analyzes the effect of conditions during the HDO experiments on the biocrude products. The primary objective was to determine the overall mass- and carbon balances and observe changes within each phase and examine the elemental composition and deoxygenation of the biocrudes to determine the biocrude quality. The study involved analyzing water, biocrude, gas, and solid samples. Both the initial and pre-treated oil samples were evaluated in the same manner in terms of elemental composition and deoxygenation as other biocrude samples.

7.1 Biocrude pre-treatment

This section details the observed yield of biocrude during pre-treatment and describes the resulting properties of the oil.

7.1.1 The yield in the pre-treatment of biocrude

The pre-treated biocrude samples underwent a filtration process to assess the solid content originally present in the biocrude and to evaluate the efficacy of the filtration when the biocrude was dissolved in IPA (isopropanol). For a better understanding of the principle evaluating and recording the data concerning pre-treated samples, parameters like the batch number, weight of the original pine biocrude, weight of the filtered solids from the pre-treating samples, and the yield percentage of the pre-treated batches were documented.

While the initial weights of the biocrude samples across different batches exhibited variations, the primary metric of interest is the yield, which offers insights into the filtration's effectiveness. The yields from the batches ranged between 67% to 87%' It's worth noting that the amount of solids removed during filtration would be influenced, in part, by the pore size of the filtration paper utilized. The subsequent (Table 18) summarized the gathered data, providing a representation of the outcomes from the filtration process when producing the pre-treated samples. The yield was determined by measuring the amount of filtered solids removed from the initial HTL biocrude. The yield was calculated by measuring the amount of solids removed following equation (13).

$$Yield\ (\%) = \frac{Initial\ HTL\ biocrude\ (g) - Filtered\ solids\ (g)}{Initial\ HTL\ biocrude\ (g)} \times 100 \tag{13}$$

Table 18. Filtration Yields and Solid Removal from Pre-treated Biocrude Samples.

Batch	Pine biocrude (g)	Filtered solids (g)	Yield (%)
1	115	23	**80**
2	109	23	**79**
3	143	26	**82**
4	107	35	**67**
5	102	32	**68**
6	103	13	**87**
7	150	37	**75**

7.1.2 The properties of pre-treated biocrude

The elemental composition of the biocrude samples shows a marked increase in carbon (C) content after pre-treatment from the original untreated HTL sample of 62.4% to values between 65.6% and 69.4% in pre-treated biocrude batches (1-7). The hydrogen (H) content also showed an increase after pre-treatment, ranging between 8 and 9% for the pre-treated batches compared to the 7.7% of the original sample. Nitrogen (N) and sulfur (S) contents remained stable in all batches. The most noticeable observation is the decline in oxygen (O) content: from 29.8% in original biocrude sample in a range of 21.5% to 26% in the pre-treated samples. The elemental composition, DOD, HHV, and ER are presented in the Table 19.

Elemental ratios (hydrogen-to-carbon) provide insights into the relative saturation of a fuel. Higher ratios often signify more saturated compounds, which can be advantageous for biofuel quality. From the data provided, the H/C ratios of the pre-treated samples range from 1.47 to 1.69, implying an increase from the original sample. The average DOD for the pre-treated samples (batches 1-7) is 19%. The average HHV for batches 1-7 is 31.2 MJ/kg. This is in stark contrast to the original batch which had an HHV of 27.8 MJ/kg. When evaluating the energy recovery (ER) for the pre-treated batches, using the HHV of the original batch as the energy input, we found that all the pre-treated batches exceeded the baseline ranging from 110.4% to 113.7%.

The pre-treatment of the pine biocrude resulted in notable improvements in its elemental composition, specifically by escalating the carbon and hydrogen contents and concurrently reducing the oxygen content. These adjustments positively impacted the biofuel quality, as evidenced by the increase in the hydrogen-to-carbon (H/C) ratios and the higher heating value (HHV), and therefore positive energy ratio values.

Table 19. Elemental Composition (C, H, N, O, S) and Properties – Elemental Ratios (C/H), Degree of Deoxygenation (DOD), Higher Heating Value (HHV) of the original pine biocrude and the batches 1-7, and Energy recovery (ER).

Batch	Elemental composition (%)					Elemental ratios (%)	DOD (%)	HHV (MJ/kg)	ER (%)
	C	H	N	O	S	H/C			
Pine Biocrude	62,4	7,7	0,1	29,8	0,009	1,47	-	27,8	-
1	69	8,2	0,1	22,7	0,03	1,56	20,5	31,4	113,0
2	67,6	8	0,1	24,3	0,02	1,69	15,4	31,2	112,2
3	68,2	8,1	0,1	23,6	0,02	1,49	21,1	31,3	112,6
4	66,4	8,7	0,1	24,8	0,02	1,52	17,1	30,7	110,4
5	68,6	8,9	0,1	22,4	0,02	1,59	15,4	30,8	110,8
6	65,6	8,3	0,1	26	0,02	1,48	23,5	31,6	113,7
7	69,4	9	0,1	21,5	0,02	1,55	20,8	31,5	113,3

7.2 Catalyst comparison experiments

Optimization of biocrude yields is central to the objective of this work, with a strong emphasis on evaluating the influence of different catalysts on the yield of upgraded biocrude. A comprehensive analysis was carried out, focusing primarily on three different catalyst types, sulfided Ru/AC, sulfided Ni/Mo and unsulfided Ru/AC, under the specified conditions of a temperature of 320°C, a pressure of 30 bar and a reaction time of 2 hours. The elemental composition, Deoxygenation Percentage (DOD) and Higher Heating Value (HHV) from these tests were examined. These parameters not only measure the efficiency and suitability of the selected catalysts, but also highlight their impact on the fuel quality and energy content of the refined biocrude product.

7.2.1 Effect of catalyst on yield

With sulfided Ru/AC, the biocrude yield obtained under the influence of this catalyst was 23.3% in terms of mass balance, which was really low. The carbon balance was slightly higher at 23.6%. The coke yield on this catalyst showed a mass balance of 13.0% and a carbon balance of 12.8%, which again is low, indicating a loss of biocrude during the experiment. The procedure for after-treating the biocrude sample had not been refined in this catalyst test yet, and it's likely that the dissolving of biocrude in the autoclave was done unsuccessfully. For this specific catalyst test, instead of using the ethyl acetate to retrieve the coke and biocrude form the autoclave, as an exception to future tests, acetone was used to retrieve the samples.

The sulfided Ni/Mo catalyst showed a significant increase in biocrude yield, with a mass balance of 52.9%. The carbon balance also increased to 54.3%. While the mass balance for coke formation was 23.5%, the carbon balance increased to 29.7%. The rise in the yield in both biocrude and coke is justified as due to a more successful sample handling and processing.

The unsulfided Ru/AC catalyst showed a biocrude yield of 55.9% in terms of mass and a slightly higher 57.4% in terms of carbon. In terms of coke formation, the mass balance was 27.8% and the carbon balance was 31.7%. The rise in the yield in both biocrude and coke is justified as due to a more successful sample handling and processing.

Mass- and carbon balance represented in Figure 29. In the figure, each bar represents different components of the mass and carbon balance resulting from the biocrude upgrading process. The yellow bar shows the mass and carbon balance for upgraded biocrude, illustrating the conversion efficiency of the biocrude into a higher quality fuel. The orange bar shows the gas production balance, demonstrating how much of the biocrude is converted to gas. The black bar focuses on coke formation, providing insight into the amount and carbon content of the solid by-product. The blue bar shows the carbon balance for water soluble products (WSP), indicating the proportion of carbon that ends up in the aqueous phase. The grey bar represents the total mass and carbon balance of the system, summarizing the overall outcome of the upgrading process.

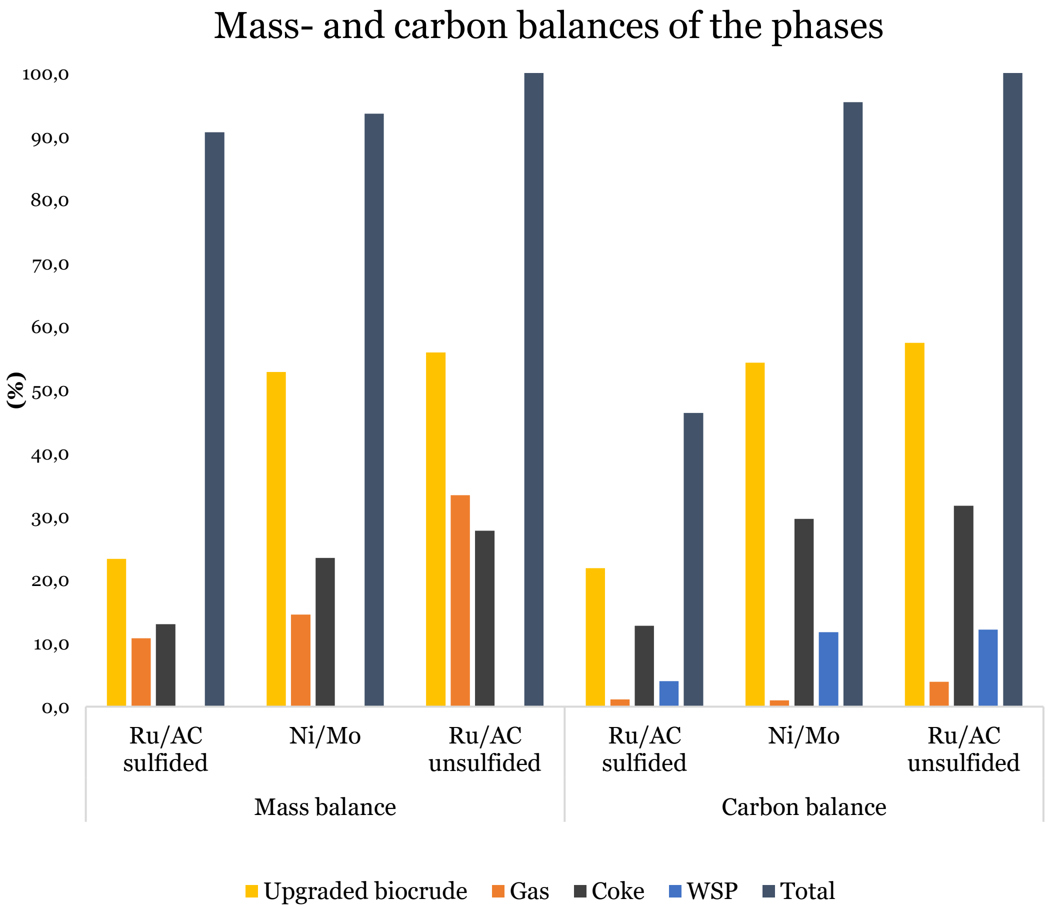


Figure 29. Comparative Mass and Carbon Balance Analysis Across Upgrading Process Phases.

Mass balance provides an overall perspective on the distribution of total reactants and products, whereas carbon balance focuses on carbon atoms. The energy content, and therefore value, of biocrude is fundamentally linked to its carbon content, so it is important to track where the carbon goes. It provides insight not only into the biocrude yield, but also into the potential energy content of the resulting biocrude. Unfortunately, achieving full closure of the mass balance proved challenging due to several potential experimental errors. These could have included unsuccessful sample recovery from the reactor, small spills of bio-oil during handling, evaporation or loss of some oil compounds during solvent removal, potential losses during pressure relief and incomplete recovery of oil slurry from the reactor walls. This was especially true for the first catalyst experiment, sulfided Ru/AC catalyst, which had slightly unconventional after-treatment handling in comparison to the unsulfided Ru/AC and sulfided Ni/Mo catalyst HDO tests. The sulfided Ni/Mo and unsulfided Ru/AC catalyst experiments showed comparable yields, particularly in terms of carbon. It's important to note that only a single test was performed for each catalyst type. Therefore, it is one should not make definitive judgements based on this limited data set.

The principle behind calculating and defining the mass and carbon balances are presented in more detail in chapter 6.5.2. (The principle of mass- and carbon balance analysis). In brief, in the mass- and carbon balance section for upgraded biocrude, gas, coke and aqueous solution/WSP, the values are compared to the original amount of biocrude used in the process to follow the phase-shifting of substances and material preservation or changes of material in those phases. The upgraded biocrude represents the yield in which the biocrude is obtained after HDO. Other values similarly show the mass change in each phase, which indicates how much from the biocrude batch sample in the beginning of the reaction was converted to that phase. The gas mass balance represents the percentual amount of weight transferred from the biocrude to the gas phase, and coke mass balance the percentual amount of biocrude transferred into coke from the biocrude. The WSP presents the percentual amount of biocrude transferred into water soluble products in the water phase from the biocrude, however this was only calculated with carbon balance. In the Table 20, in the on mass balance section there is aqueous solution instead of WSP. In the case of water samples, the results are confusing due to the variable loss of water experienced during the experiments. In the table 20, aqueous solution presents the percentual change in water from the beginning of the reaction to the end of the reaction, in other words, shows how much of the original water remained and was recovered after the test (yield). This loss of water and leakage was a major problem and is discussed in the Chapter 7.5.3 (Experimental limitations).

Table 20. Mass and Carbon Balance Distribution across Different phases - Upgraded Biocrude, Gas, Solids, Aqueous solution (△), and Water-Soluble Products (WSP).

Catalyst	**Reaction conditions**			**Experiment**			**Mass balance (%)**					**Carbon balance (%)**				
	Temperature (°C)	Pressure (bar)	Time (h)	Test	ID	Batch	**Upgraded biocrude**	Gas	Coke	Aqueous solution (△)	Total	**Upgraded biocrude**	Gas	Coke	WSP	Total
Ru/AC sulfided	320	15	2	1	69	2	**23,3**	10,8	13,0	-5,0	90,7	**23,6**	1,1	12,8	11,7	46,4
Ni/Mo sulfided	320	5	2	2	70	2	**52,9**	14,5	23,5	-45,5	93,6	**54,3**	1,0	29,7	11,4	95,4
Ru/AC unsulfided	380	5	2	3	71	3	**55,9**	33,4	27,8	1,8	102,1	**57,4**	3,9	31,7	12,1	101,3

7.2.2 Catalyst effect on properties of the oil

Original biocrude

The analysis of the elemental composition of pine biocrude was performed for the biocrude sample before pre-treating the sample or upgrading it via HDO. The original pine biocrude sample has a carbon content of 62.4%, a hydrogen content of 7.7%, a very low amount of nitrogen content of 0.1%, an oxygen content of 29.8% and a sulfur content of 0.009%. The higher heating value (HHV) of the original biocrude is 27,8 MJ/kg. This analysis sets the baseline for subsequent comparison in catalyst and studying the effect of conditions as well. The results for the studied elemental composition and properties of the biocrude represented in Table 21.

Pre-treated biocrude

When the original pine biocrude is compared with the pre-treated batch (1), there is an increase in the elemental composition and improvement in the quality of the oil in terms of deoxygenation. The pre-treated sample shows a carbon content of 67.4%, hydrogen at 8.8% and oxygen reduced to 23.7%. This increase in the H/C ratio to 1.56 suggests an enrichment of the hydrogen content in relation to its carbon. The higher heating value (HHV) is noted at 31.4 MJ/kg, with some increase from the original pine biocrude sample.

Sulfided Ru/AC treated biocrude

Sulfided Ru/AC catalyst has a composition very similar to the pre-treated batch. It has a slightly increased carbon concentration of 68.2%, by a reduced hydrogen content of 8.3%. The deoxygenation degree (DOD) is only 1.3%, indicating a minimal reduction in oxygen content. This results in a slightly reduced H/C ratio of 1.45 and a HHV of 31.2 MJ/kg, which is not very different from the unupgraded pre-treated sample.

Sulfided Ni/Mo treated biocrude

The performance of the sulfided Ni/Mo catalysts carbon content reaches 69.4%, with a hydrogen content of 8.1% and the biocrude has a more noticeable oxygen reduction (DOD) of 5.6%. H/C ratio sets to 1.39 and the HHV is 31.5 MJ/kg. Although the sample has a slight change in oxygen level, the HHV does not show any markable change.

Unsulfided Ru/AC treated biocrude

The unsulfided Ru/AC catalyst has the highest carbon concentration of catalyst tests at 70%, and with a hydrogen content of 8.7%. DOD is significantly enhanced to 10.6%, indicating significant deoxygenation. Its H/C ratio remains consistent with the original pine biocrude at 1.48 and it has the highest HHV of 32.5 MJ/kg.

Table 21. Elemental Composition (C, H, N, O, S) and Derived Properties of biocrude samples for catalyst testing – Elemental Ratios (C/H), Degree of Deoxygenation (DOD), and Higher Heating Value (HHV)

Catalyst	**Reaction conditions**			**Experiment**			**Water con-tent (%)**	**Elemental composition (%)**					**Elemental ratios (%)**	**DOD (%)**	**HHV (MJ/kg)**
	Tem-pera-ture (°C)	Press (bar)	Time (h)	Test	ID	Batc h		C	H	N	O	S	H/C		
-	Pine biocrude (Original sample)						-	62,4	7,7	0,1	29,8	0,009	1,48	-	27,8
-	Pre-treated Batch					1	0,8	67,4	8,8	0,1	23,7	0,009	1,56	20,5	31,4
Ru/AC sulfided	320	30	3	1	69	1	0,2	68,2	8,3	0,1	23,4	0,024	1,45	1,3	31,2
Ni/Mo sulfided	320	30	3	2	70	1	1,1	69,4	8,1	0,1	22,4	0,024	1,39	5,6	31,5
Ru/AC unsulfided	320	30	3	3	71	1	0,2	70	8,7	0,1	21,2	0,024	1,48	10,6	32,5

Analysis of these results showed that all catalysts improved the elemental composition of the bio-crude compared to the pre-treated and original sample very moderately. The unsulfided Ru/AC stood out slightly in terms of deoxygenation and energy content (HHV). However, it is also worth noting the similarity of results between the untreated batch and the catalyst tests. This observation points that the pre-treatment itself was effective. The impact of pre-treating the sample showed more change than the reaction itself in terms of deoxygenation.

This investigation has demonstrated the performance of the catalysts under consistent conditions. Although the sulfided Ni/Mo catalyst and unsulfided Ru/AC showed close results, it is important to treat such findings with caution given the single-test nature of the data set. Due to a lack of time to perform more tests with the catalysts and to analyze the catalysts more thoroughly with more repetitions, further primary experiments and analysis regarding effect of conditions (7.4) were carried out using the sulfided Ru/AC catalyst mainly due to supplier Ranido's stability performance tests and the literature review regarding ruthenium catalyst.

7.3 Sample phase characterization and analysis

In this chapter, we explore the detailed analysis of different sample phases, including water, biocrude, and solid samples. After the HDO test performed for catalyst comparison tests and experiments studying the effect of conditions, the samples were storage and send for analyzation. Each biocrude and water sample was placed into 22 ml vials, and the solids were moved in sealed plastic bags. The samples were sent to three distinct facilities: Bioruukki VTT, Aalto University, and Eurofins Jyväskylä. The choice of facility for each sample was based on the specific type of analysis needed and the expertise and equipment available at each location. This strategic distribution was crucial for obtaining accurate and relevant analytical results for each sample type; water, biocrude, and solids. To understand the analysis methods, the chapter 6.5 (Analyses) provides the analyses in detail.

7.3.1 Biocrude Samples

The biocrude samples were examined at two key stages: before and after the hydrodeoxygenation (HDO) process, each exhibiting unique characteristics. The samples before HDO were the pre-treated "batch" biocrudes used in the HDO reaction. The samples after the HDO were analyzed after removing them from the autoclave post to the after-treatment, which allowed us to retrieve more sample from the reactor. The original biocrude was also analyzed but it is presented in the materials section in chapter 5.2.1 (HTL biocrude). All biocrude samples were analyzed using KF-titration to determine water content, CHN-analysis for elemental analysis, and few samples were used to analyze sulfur content.

Pre-treated Biocrude Samples:
Initially, these samples were thick and solid-like, presenting significant handling challenges. To address this, the samples were treated with isopropanol (IPA), which was later evaporated. This treatment significantly reduced the viscosity, making them easier to handle and process. It's important to note that despite the evaporation, traces of IPA might still have remained in the samples. These pre-treated samples served as a reference for comparing with the reactor test samples (Figure 30). A key procedure during this stage was the removal of solids, which facilitated subsequent processing.

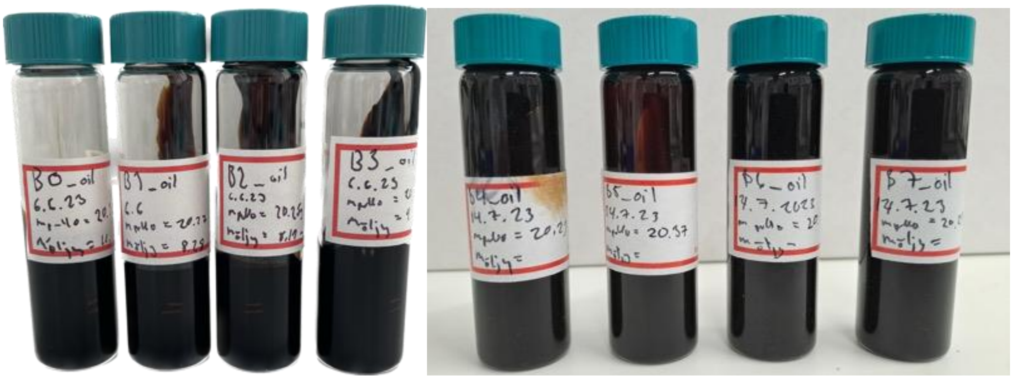


Figure 30. The IPA treated and first phase filtrated biocrude samples (Batch 0, 1, 2, 3, 4, 5, 6, and 7).

Post-HDO Biocrude Samples

Following the HDO process, the biocrude changed dramatically. After evaporating the ethyl acetate, the biocrude resulted in a more liquid-like substance. This transformation made handling challenging due to the increased fluidity. Additionally, the yield of these post-HDO samples was notably low, necessitating careful handling to minimize losses. These samples, particularly those from higher temperature reactions, exhibited lower viscosity and potentially fewer solids, suggesting a higher purity level. Similarly, as with pre-treated samples, there is a possibility that residual solvent ethyl acetate could have remained, influencing the samples' properties. The upgraded samples are presented in Figure 31 and Figure 32.

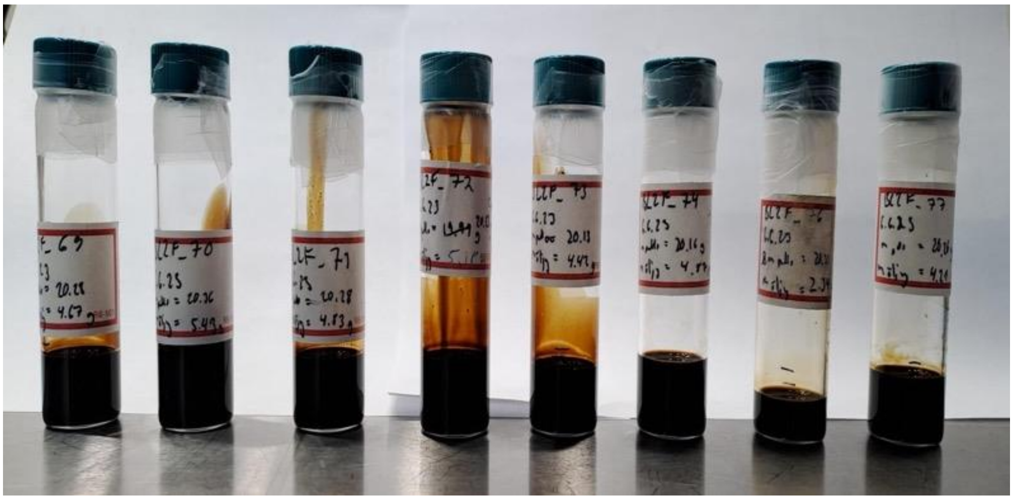


Figure 31. The biocrude samples from the performed experiments (68-77).

Figure 32. The biocrude samples from the performed experiments (79-88).

7.3.2 Water Samples

The water samples were attained after each HDO experiment from the reactor autoclave by pouring the separated water phase apart to their own container, in which the samples were weighted in and preserved in cold. When moving the samples for analysis, a part of the water phase was transferred into vials before packaging and sending them to be analyzed. The water samples were analyzed using total carbon analysis and KF-titration. Some minor color variations were observed in these samples, which appeared to be closely linked to the conditions of the reactions. Notably, samples that were subjected to higher temperatures were clearer compared to those at lower temperatures. This increased clarity at higher temperatures is likely a result of better separation between oil and water or possibly the solidification of the oil. This finding is particularly significant because the water samples were not filtered, making the clarity a direct indicator of the reaction conditions. These observations are visually represented in Figure 33 and Figure 34.

Figure 33. The water samples from the performed experiments (68-77).

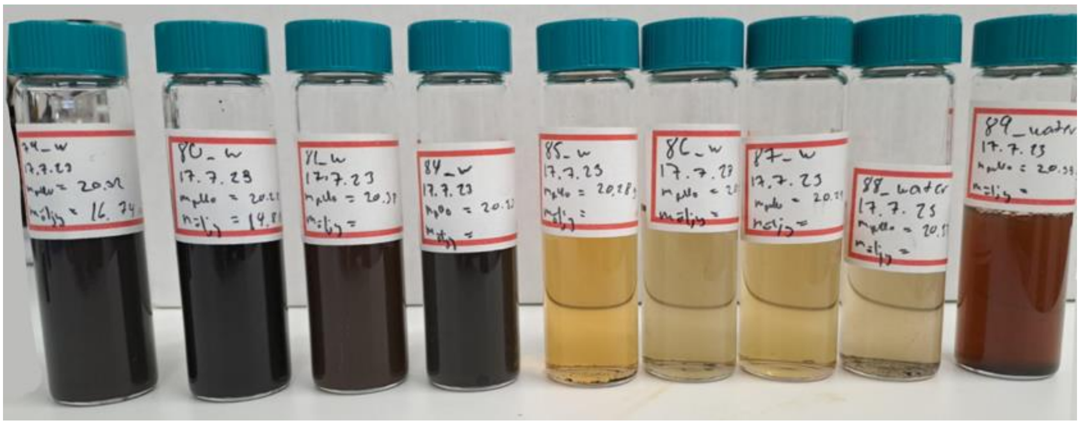


Figure 34. The water samples from the performed experiments (79-89).

7.3.3 Solid Sample Analysis

Our study included an examination of solid samples, for the pre-treatment solids before HDO, and for solids post-HDO stages in terms of yield and the quality of the solids. Solid samples after the reaction were subjected to CHN-analysis performed by Bioruukki laboratory.

Pre-treated Solid Samples

During the pre-treatment phase, the aim was to reduce the viscosity of biocrude by removing the solids from the original biocrude. The solids were collected from the filtered material. These samples, mostly resembling graphite in texture, were obtained by filtering the IPA-dissolved biocrude (Figure 35). Sufficient drying time was allowed before collection of the solid samples and analysis. Some challenges were encountered during the filtration process. In some instances, the filtration was disrupted, resulting in reduced suction of the suction filter and potentially incomplete separation. This issue could have affected the consistency and quantity of the filtered solids, but it is believed not to have significantly impacted the overall substance compared to that successfully filtered ones. In scenarios of reduced suction, the suction rate could be reduced to the point where the filtered paper is not intact, and the material is dispersed around the filter paper. Based on the yield data (Table 18) in the biocrude pre-treatment table, there is a strong suspicion that this occurred in one of the tests with lower solid content measured in the filtration.

Figure 35. The solid samples from the IPA filtration (Batch 1, 2, 3).

Post-HDO Reaction Coke & Catalyst Samples

After the HDO process, the focus was on the coke and catalyst samples filtered from the biocrude. The coke, a waste material produced during the reaction, was separated from the biocrude along with catalyst using ethyl acetate, followed by filtration. The coke, especially from higher temperature reactions, tended to be finer and more abundant than that from lower temperatures. The samples were weighed before and after the process to evaluate the residual coke and catalyst content, providing a quantitative measure of these components (Figure 36).

Figure 36. Post HDO filtered coke sample.

7.4 Impact of Varied Upgrading Conditions on Product Yield and Characteristics

A series of HDO experiments were carried out using a sulfided ruthenium activated carbon (Ru/AC) catalyst in order to optimize the quality of the biocrude, in particular its degree of deoxygenation and energy content. Various parameters such as reaction temperature, pressure and time were adjusted and their effects were evaluated in terms of mass- and carbon balance, elemental composition, degree of deoxygenation (DOD) and high heating value (HHV) in the biocrude samples. By analyzing each parameter in relation to the test data, the optimal conditions for the HDO reaction could be determined. It is worth noting that the results are a combination of three factors: temperature, pressure and duration of the HDO reaction. The theory behind the execution of mass- and carbon balance calculation is introduced in chapter 6.5.2 (The principle of mass- and carbon balance analysis) and discussed also in chapter 7.2.1 (Effect of catalyst on yield).

7.4.1 Effect of conditions on yields on product factors

This section presents and discusses the results regarding mass- and carbon balances and the effect of conditions in HDO. The mass- and carbon balances of the HDO experiments are represented below in the Figure 37 and Figure 38. In the figures 37 and 38, the mass- and carbon balances of the phases are presented similarly as in the chapter 7.2.1 (Effect of catalyst on yield), along with process conditions. This summarizes the effect of the upgrading process conditions of temperature, pressure, and time. The full data is represented in Table 22.

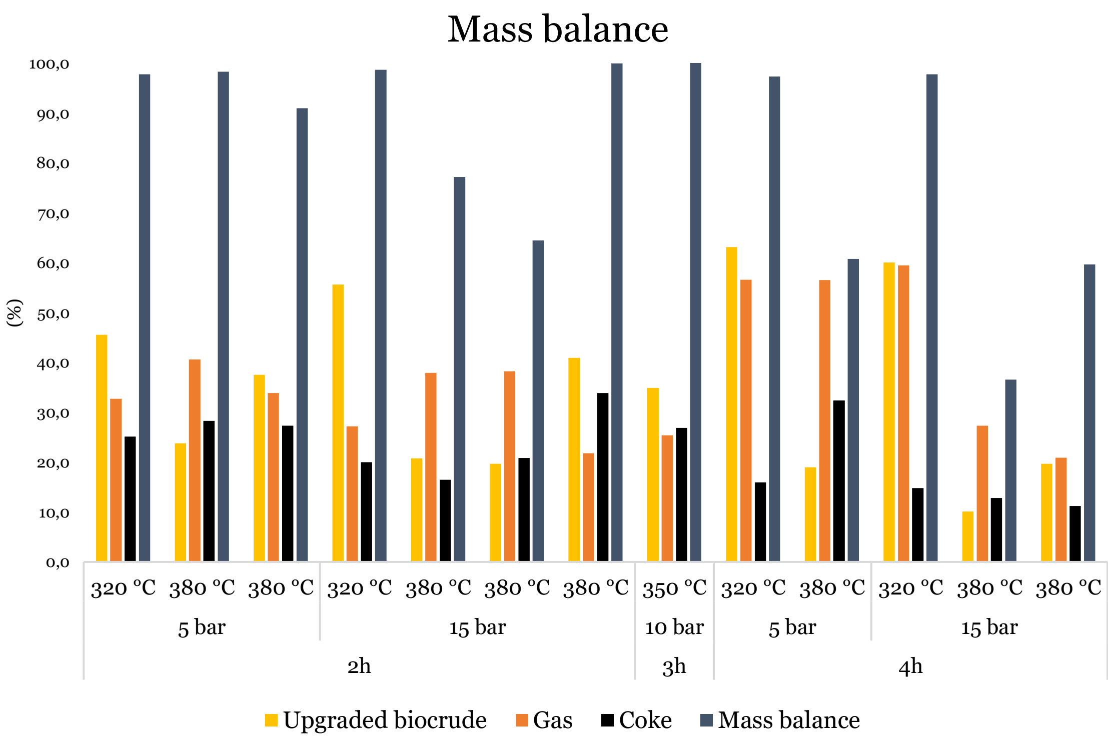


Figure 37. Bar Chart Analysis of Upgraded Biocrude, Gas, Coke, and for Mass balance.

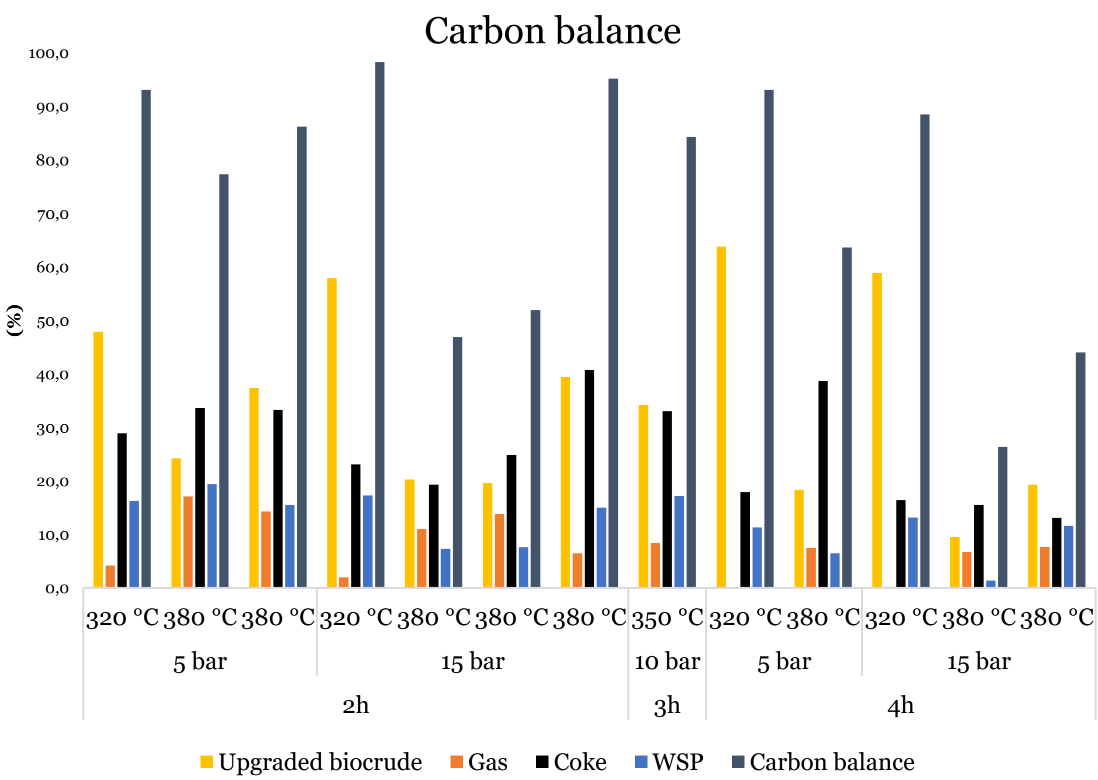


Figure 38. Bar Chart Analysis of Upgraded Biocrude, Gas, Coke, and WSP for Carbon balance.

Upgraded biocrude

Temperature was a dominant factor in determining biocrude yield. At 320°C, biocrude production ranged from 19.7% to 63.2%, with an average yield of 40.8%. On the other hand, at the increased temperature of 380°C, the production ranged widely from 10.1% to 41.0%, with a significant decrease in the average yield to 25.3%. As an example, at a hydrogen pressure of 5 bar and a reaction time of 2 hours, the upgraded biocrude yield decreased sharply from 45.6% at 320°C to 23.8% at 380°C in the matter of mass balance. The carbon balance reflected this decrease from 47.9% to 24.2%. The overall averages clearly showed that the experiments conducted at 320°C yielded significantly higher biocrude yields than those conducted at 380°C. This supports the hypothesis that higher temperatures may increase gas and coke formation, thereby limiting biocrude production.

Initial hydrogen pressure in the beginning was found to have an effect on biocrude yield. A specific case at 320°C over a period of 2 hours showed that by escalating the hydrogen pressure from 5 bar to 15 bar, there was a favorable improvement in the mass balance yield from 45.6% to 55.6%. The carbon balance showed an increase from 47.9% to 57.9%. It is important to note that the correlation between pressure and yield was not consistently linear across all temperature variations, highlighting the complex interdependency between pressure and temperature dynamics.

To illustrate the effect of time, when conditions were set at 320°C and 15 bar, extending the reaction interval from 2 to 4 hours promoted an increase in biocrude yield from 55.6% to 60.1% according to the mass balance. At the same time, the carbon balance reflected a more modest increase from 57.9% to 58.9%. It became clear however, that longer times didn't always increase yields across the whole range of temperature and pressure settings, making reaction time a slightly unpredictable parameter based on the tests.

Gas formation

The effect of temperature showed that at a lower temperature of 320°C, the carbon transfer to the gas phase was quite limited, averaging only about 1.6%. At a higher temperature of 380°C, there was a significant increase in carbon transfer to the gas phase, averaging around 11.4%. This shows that higher temperatures were more effective for transferring carbon to the gas phase., which could mean that volatile components were formed from the biocrude.

At 5 bar pressure, the average carbon in the gas phase was around 7.2%. When the pressure was increased to 15 bars, the average carbon in the gas phase was slightly lower, at 6.9%. This could suggest that higher pressure in the beginning didn't increase the transfer of carbon to the gas phase. But difference between pressure values in total conditions is quite small and the tha change low as well.

For reactions lasting 2 hours an average of 9.6%, was transferred to the gas phase. However, when extending the reaction time to 4 hours the average carbon in the gas phase reduced to 3.8%. This is contradictory. The gas phase should not reduce with the longer tests, especially at this level. It should be noted here that a leakage was noted from the recoded reaction condition data. The reason for decrease in carbon content in the longer reaction duration could be that the amount of gas lost in the longer reaction time would contribute to more leakage, resulting in the reduction in gas content and carbon in that gas phase. The same could apply when increasing the hydrogen load, with a hypothesis that higher pressure would promote more leakage and therefore a reduction of the transferred matter in the gas phase.

WSP

In water soluble analysis the carbon change from biocrude to water phase was measured and is shown only for the carbon balance analysis. At a lower temperature of around 320°C, the average carbon balance was around 14.5%. To clarify, this means that when measuring the carbon transfer to the water phase in the reaction, in this case 14.5% of the mass of the carbon in the biocrude placed into the reaction before the reaction was transferred to the water phase. This was to follow the movement of carbon one phase to another. Carbon balance of 11.8% was found in the higher temperature tests at 380°C. It should be noted that hypothetically, higher leakage at higher temperature and pressure range would reasonably result in lower water recovery and therefore lower number of carbon estimated after the reaction. The amount of WSP could actually be higher without leakage and water loss with tests, especially with higher temperature experiments.

The data showed that at 5 bar pressure, the average carbon balance in the WSP was around 13.8%. Increasing the pressure to 15 bar resulted in a lower average carbon balance of approximately 11.9%. This would suggest that higher pressure does not initially improve carbon retention in the WSP, but on the other hand, water loss could also be behind the reduction.

For reactions lasting 2 hours, an average of 14.1% carbon was retained in the WSP. However, when the reaction time was increased to 4 hours, the average carbon balance in the WSP decreased to 10.8%. In this case, it could again make sense to transfer more biocrude to the water solution with a longer reaction time, but the data and the reduction in WSP suggest that increased duration may be more efficient in retaining carbon in the biocrude in these tests. The leakage and loss of water sample are likely reasons for this occurrence. There is similar correlation with the time related reduction of carbon content in the gas and WSP.

Coke

It was found that at a lower temperature of 320°C, coke formation was with an average mass balance of about 19.0% and a carbon balance of about 21.6%. At a higher temperature of 380°C, there was an increase in coke formation with an average coke mass balance of 23.9% and carbon balance of 27.1%.

This indicates that higher temperatures lead to more coke formation, both in terms of mass and carbon content.
At 5 bar pressure, the coke phase was significantly formed with an average mass balance of 25.8% and a carbon balance of 30.5%. Increasing the pressure to 15 bar resulted in slightly lower levels of coke formation, with an average mass balance of 19.7% and carbon balance of 21.5%. This could suggest that higher initial hydrogen pressure load decreased coke formation.
For reactions lasting 2 hours, the average mass balance was 24.6% and the carbon balance was 29.1%. Extending the reaction time to 4 hours resulted in slightly lower levels of coke formation, with an average mass balance of 19.1% and carbon balance of 19.8%. This suggests that longer reaction times may result in less coke formation. Mass- and carbon balances are represented in the Figure 38 and the full outcomes of the experiments and the data are presented in Table 22.

The tests marked as number 9 and 14 showed irregularities in terms of significant pressure leakages and biocrude yield their exclusion from the primary analysis. The deviation observed for the mass- and carbon balances, could have been related to abnormal leakage discovered during the pressure studies, which are thoroughly analyzed in Chapter 7.5.3 (Experimental limitations). It is important to emphasize that the averages presented do not incorporate data from 9 and 14 due to their atypical outcomes. The exclusion resulted in slight alterations to the average values. Especially the last test had different characteristics, which can be seen better in the next chapter that presents the properties of the oil. The effect of the unintended pressure changes during the reaction could relate to the deviations within phases and preservation of water (aqueous solution) in the reaction. Some correlation can be found with the amount of water lost in the reaction and how much the pressure changed during the reaction.

Table 22. Comparative Mass and Carbon Balance Distribution Across Different –phases - Upgraded Biocrude, Gas, Solids, Aqueous Solution (△), and Water-Soluble Products (WSP) under Various Upgrading Conditions.

Reaction conditions			**Experiment**			**Mass balance (%)**					**Carbon balance (%)**				
Temperature (°C)	Pressure (bar)	Time (h)	Test	ID	Batch	Upgraded biocrude	Gas	Coke	Aqueous solution (△)	**Total**	Upgraded biocrude	Gas	Coke	WSP	**Total**
320	15	2	1	72	2	55,6	27,2	20,0	-15,8	98,7	57,9	2,0	23,1	17,3	98,3
320	5	2	2	73	2	45,6	32,7	25,2	96,8	97,8	47,9	4,2	28,9	16,3	93,1
380	5	2	3	74	3	23,8	40,6	28,3	95,0	98,3	24,2	17,1	33,7	19,4	77,3
380	15	2	4	76	3	20,8	37,9	16,5	100,2	77,2	20,3	11,0	19,3	7,3	46,9
380	15	2	5	77	3	19,7	38,2	20,8	76,7	64,5	19,6	13,8	24,8	7,6	51,9
320	15	4	6	79	4	60,1	59,5	14,8	55,6	97,8	58,9	0,2	16,4	13,2	88,5
320	5	4	7	80	4	63,2	56,6	16,0	89,7	97,4	63,8	0,0	17,9	11,3	93,1
380	15	4	8	81	4	10,1	27,3	12,8	95,1	36,6	9,5	6,7	15,5	1,4	26,4
350	10	3	9	84	5	34,9	25,4	26,9	32,5	103,7	34,2	8,4	33,0	17,2	84,3
380	5	2	10	85	5	37,5	33,9	27,3	105,4	91,0	37,4	14,3	33,3	15,5	86,2
380	15	2	11	86	6	41,0	21,8	33,9	91,7	100,0	39,4	6,5	40,7	15,0	95,2
380	5	4	12	87	6	19,0	56,5	32,4	91,6	60,8	18,4	7,5	38,7	6,5	63,6
380	15	4	13	88	7	19,7	20,9	11,2	56,7	59,7	19,3	7,7	13,1	11,6	44,0
350	10	3	14	89	7	13,7	60,0	34,8	31,8	48,1	9,0	14,7	42,1	12,5	52,2

7.4.2 Effect of experimental conditions

This section analyzes the effect of different HDO reaction conditions on the properties and characteristics of biocrude using a sulfided Ru/AC catalyst. The parameters considered were temperature, pressure, and time and their influence on the elemental composition, degree of deoxygenation (DOD), and higher heating value (HHV) of the biocrude. The data is presented in Table 23.

Elemental composition

The analysis showed that the carbon content of the biocrude varied with temperature, with higher carbon contents at higher temperatures. For example, at 320°C the carbon content ranged from 68.2% to 69%, while at 380°C it ranged from 66.4% to 69.4%. The hydrogen content also showed a slight increase with higher temperatures, suggesting changes in the degree of hydrogenation of the biocrude.

Degree of Deoxygenation (DOD)

Deoxygenation (DOD) is a key indicator of the quality of upgraded biocrude, as lower oxygen content results in higher heating value and better combustion properties. DOD percentages varied across the tests with an average of approximately 0.04%. The low average indicates a very limited deoxygenation effect under the given reaction conditions. Some tests at higher temperatures showed negative values. DOD values were highly sensitive and varied from test to test even when using constant operating parameters. Increasing the temperature from 320°C to 380°C at a constant pressure and time did not result in an increase in oxygen removal.

Higher Heating Value (HHV)

The HHV represents the energy density of the biocrude and is a critical factor in assessing the viability of the biocrude as a potential fuel source. The average HHV of the biocrude samples was found to be around 31.15 MJ/kg. The HHV did not show a significant variation with changes in temperature or pressure, suggesting that the energy content of the biocrude was relatively stable under the range of conditions tested.

Table 23. Comparative Analysis of Elemental Composition (C, H, N, O, S) and Derived Properties – Elemental Ratios (C/H), Degree of Deoxygenation (DOD), and Higher Heating Value (HHV) Under Varied Upgrading Conditions.

Reaction conditions			**Experiments**			**Water content (%)**	**Elemental composition (%)**					**Elemental ratios (%)**	**DOD (%)**	**HHV (MJ/kg)**
Temperature (°C)	Pressure (bar)	Time (h)	Test	ID	Batch		C	H	N	O	S	H/C		
320	15	2	1	72	2	0,4	68,2	8,1	0,1	23,6	0,02	1,48	6,3	30,9
320	5	2	2	73	2	0,3	69	8,2	0,1	22,7	0,03	1,42	9,9	31,4
380	5	2	3	74	3	0,3	69,4	9	0,1	21,5	0,02	1,42	8,5	32,6
380	15	2	4	76	3	1,5	66,4	8,7	0,1	24,8	0,02	1,55	-5,5	30,9
380	15	2	5	77	3	0,2	68,6	8,9	0,1	22,4	0,02	1,56	4,7	32,1
320	15	4	6	79	4	0,3	65,6	8,3	0,1	26	0,02	1,55	-5,3	30,0
320	5	4	7	80	4	0,2	67,6	8	0,1	24,3	0,02	1,51	1,6	30,5
380	15	4	8	81	4	0,4	62,5	8,8	0,1	28,6	0,02	1,41	-15,8	29,2
350	10	3	9	84	5	0,2	64,8	8,7	0,1	26,4	0,02	1,68	-4,8	30,1
380	5	2	10	85	5	0,2	65,9	8,9	0,1	25,1	0,02	1,60	0,4	30,9
380	15	2	11	86	6	0,2	66,2	8,9	0,1	24,8	0,02	1,61	-8,8	31,0
380	5	4	12	87	6	0,2	66,9	9,2	0,1	23,8	0,02	1,60	-4,4	31,7
380	15	4	13	88	7	0,2	66,5	9,3	0,1	24,1	0,02	1,64	-2,1	31,7
350	10	3	14	89	7	40,2	44,2	9,5	0,1	46,2	0,02	2,56	-95.76%	21,8

The test sample 14 differed considerably in composition from the other samples. Laboratory tests revealed a high water content, raising questions about when the water had entered the sample. The same sample was transported to be analyzed for its sulfur content before being sent for elemental analysis. It is unclear when the sample may have been compromised. It is possible that the sample was compromised during transfer, at the start of sampling from the reactor, or during storage. The samples were preserved in the refrigerator, and the moisture could play a part. The other samples before the last test (14) were of similar quality with each other And did not exhibit higher water content. The reactor conditions also had minimal impact on the oil's properties. However, the most likely reason for the water to enter the sample would be in the water separation part post reaction.

7.4.3 Correlation Analysis of Key Factors Affecting Yield and Deoxygenation in conditional tests

The correlation between factors is evaluated in this chapter. MODDE software was used to give the reader a more robust conclusion. Figure 39 shows the effect of different conditions on yield and deoxygenation.

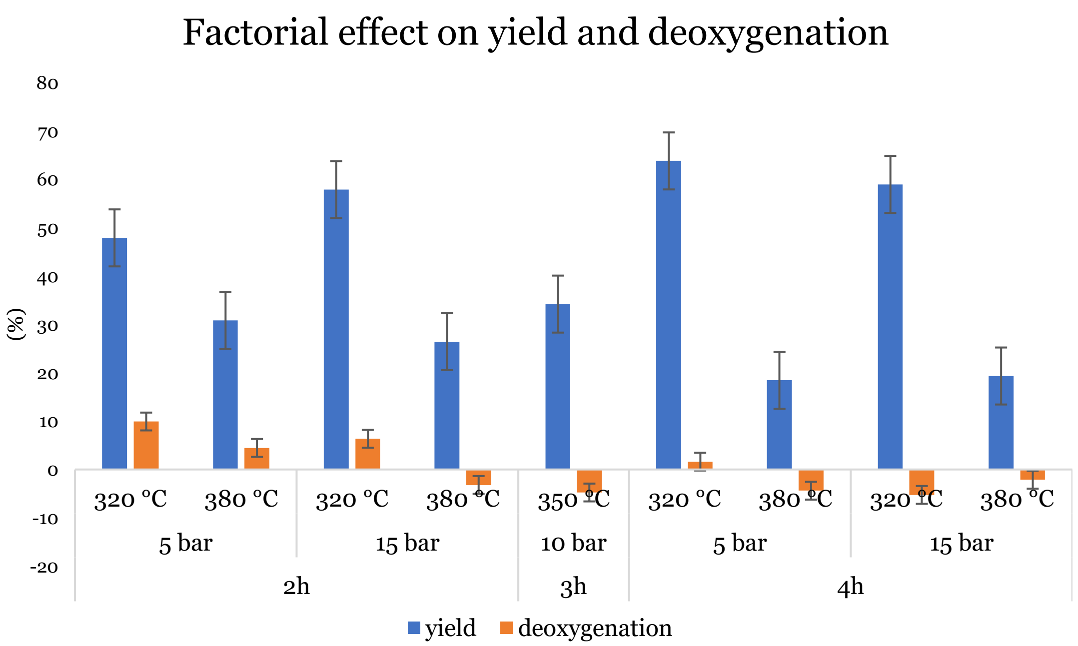


Figure 39. Factorial effect on yield and deoxygenation.

MODDE analysis software uses Variable Importance in Projection (VIP) as a tool to rank and prioritize variables based on their significance. The models in the Figure 40 provide us with a set of coefficients for each variable that influences biocrude yield and deoxygenation efficiency. The coefficients have been scaled and centered based on VIP and coefficient scores. These coefficients represent the standardized and centered values of variables' importance in a statistical model and are essential in regression analysis as they quantify the relationships between predictor variables and the response variable. They aid in understanding the value of each variable and assessing the significance of variables in the model.

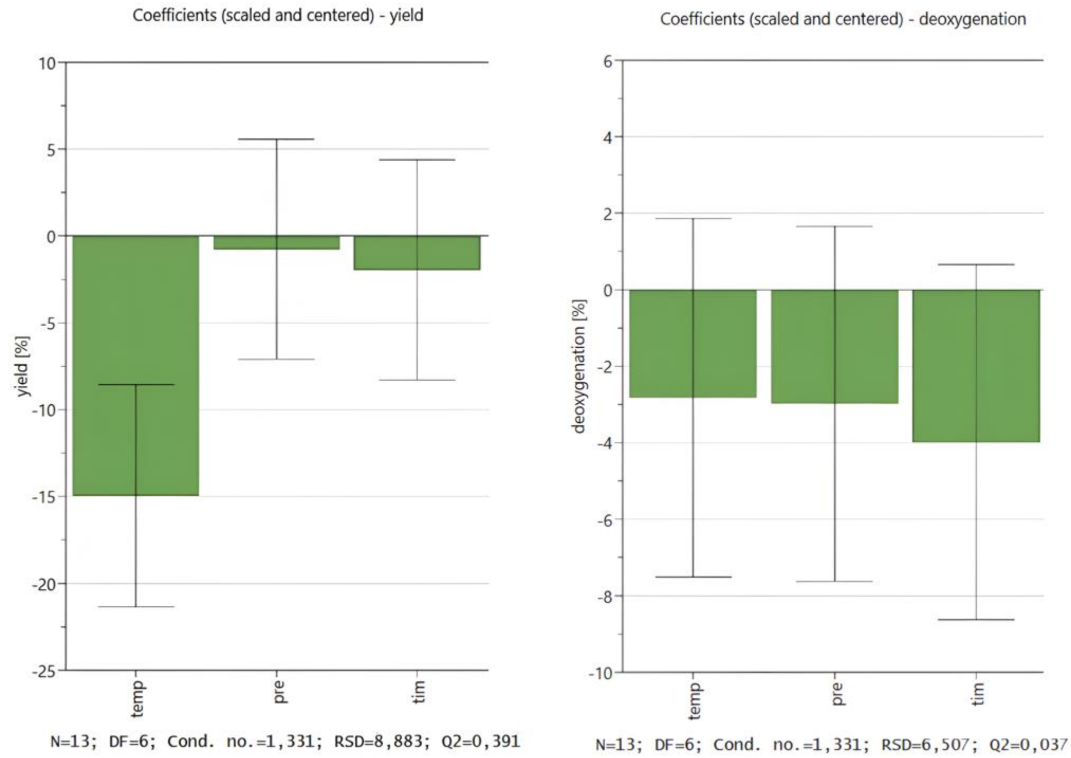


Figure 40. Coefficients for yield and deoxygenation.

The analysis revealed that the error bars were significantly larger than the coefficient bars, affecting biocrude yield and deoxygenation efficiency. Error bars represent the variation or uncertainty in our estimates. High error bars in relation to the coefficients was especially true for combined variables. High variability or uncertainty in estimates can significantly impact the reliability and interpretability of our findings. This suggests that our estimates' precision is low, making it challenging to draw firm conclusions.

Looking at the VIP data (Table 24) for yield and deoxygenation, temperature significantly reduces yield and time has a large negative impact on deoxygenation efficiency. Pressure also reduces both yield and deoxygenation, but to a lesser extent than temperature or time. The interaction effects are less clear, with temperature and pressure and temperature and time interactions showing negative effects on yield and mixed effects on deoxygenation. Cumulative (CUM) VIP scores are calculated by summing up the individual VIP scores for each variable from a multivariate model. This will give an overall measure of the variables' importance in the model, taking into account their combined effects on the response variable or the variation explained by the model.

Table 24. VIP data on yield and deoxygenation.

	VIP (cum)	**Coeff**	**VIP (cum)**	**Coeff**
	Yield	**Yield**	**Deoxygenation**	**Deoxygenation**
Temperature	2,2	-14,9	1,2	-2,8
Pressure	0,5	-0,8	1,5	-3,0
Time	0,3	-2,0	1,6	-4,0
Temp*Press	0,2	-2,0	0,1	-0,2
Temp*time	0,9	-5,3	0,2	0,7
Press*Time	0,4	-1,2	0,1	0,2

The VIP scores tell us that temperature is a key player for yield, while time seems to have the most negative effect on deoxygenation. The large error bars in previous analyses indicate uncertainty in these estimates, which means we should be cautious about how much we rely on these figures. When we look at the summary of fit (Figure 41) graphs summarizing our statistical models for biocrude yield and deoxygenation efficiency, we see how well these models are performing.

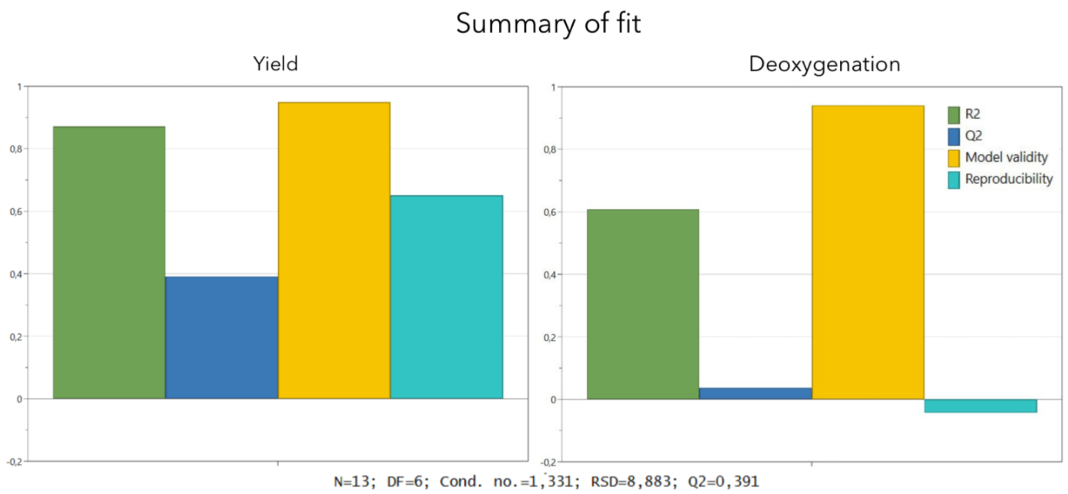


Figure 41. Summary of fit for yield on the left and deoxygenation on the right. Green bar presents R-squared (R2), Blue bar presents Q-squared (Q2), Yellow bar presents Model validity, and Turquoise presents Reproducibility.

Overall, the analyses suggest that higher temperature, pressure and processing time reduce biocrude yield, while their influence on deoxygenation efficiency is more unclear. For yield the model seems to have a good grasp on the data collected so far, which is indicated by a relatively high green bar, R-squared (R2). The R2 measures how much of the response variable's variability is explained by the model. It ranges from 0 to 1, with higher values indicating a better fit. A higher R-squared value means a higher percentage of explained variation. This is an indication that the variables selected, such as temperature, pressure, and time, have a relationship with the yield, but less so with the deoxygenation.

Q-squared (Q2) represents a key measure of the model's predictive performance. The closer Q2 values are to 1, the better the model is at predicting new data points. The Q2 value is much lower for both yield and deoxygenation, which means it is not good at predicting new data. Yield has some predictivity, while deoxygenation is close to zero.

Reproducibility measures the ability of the model to accurately reproduce observed data and assesses the extent to how well the model can mimic the data. In terms of reproducibility, which is whether we can expect the same results if we run the same process again under the same conditions, the model performs moderately well for yield. In terms of deoxygenation the number is zero.

Model validity is an evaluation of how well the statistical model aligns with the data and whether the model assumptions are met. The model validity scores for yield and deoxygenation are high. The summary of fit model fails to predict outcomes consistently. This suggests that the model aligns closely with experimental data but needs improvement to be more reliable. The model can explain a significant portion of the data's variability, with R2 values for yield and deoxygenation. It has limitations in experimental variability, especially in hydrodeoxygenation. Despite the challenges the model is well-tuned to the parameters and processes that determine yield outcomes.

7.5 Limitations and sources of error

In this chapter, we will examine the limitations and potential errors that was encountered during our HDO experiments. Each subsection will discuss different factors that may have influenced the results.

7.5.1 Methodological

There could be a potential inconsistency in the quantity or quality of pine biocrude used in different batches. There was some variation in the amount of solvents used to dissolve the biocrude oil, which could lead to inconsistent results. However, the isopropanol and ethyl acetate were used in excess to minimize the possibility of poor dissolution. The evaporation of IPA was carried out similarly at the same under-pressure value during the use of rotavapor and it was checked whether the samples lost mass.

Although standard proportions of pre-treated biocrude, catalyst and water were measured in the test, this varied very slightly from test to test. Variability in quantities, mixing procedures or even the distribution of catalyst particles could lead to uneven reactions. The mixing during the HDO reaction was set to a constant value but as discussed further, other aspects could affect the mixing.

Removal of the post-reaction phases from the autoclave presents a methodological challenge, especially given the solid nature of the oil phase. If the dissolution of the oil and coke in ethyl acetate is not consistent across runs, this could lead to variability in recovery and separation efficiencies. The filtration of the dissolved oil and coke from ethyl acetate and the separation of the oil from the solids (coke and catalyst) are steps with potential inconsistencies. The efficiency of the filtration, the retention of the oil on the filter media or even the potential degradation of some components under the influence of ethyl acetate could introduce variability in the primary biocrude studied.

One of the major limitations causing problems with the test and the lack of variability in the tests would be the volume of biocrude produced. The quantities produced were minimal, which increased the effect of error. In such small-scale reactions, any small deviation in measurement, procedural inconsistency or equipment precision can result in disproportionately large percentage errors. This sensitivity to error can affect the reliability of the data and the reproducibility of the results, making it difficult to draw definitive conclusions or to compare with larger scale studies.

7.5.2 Data limitations

Incomplete data

Pre-treatment phase

In the initial steps where biocrude oil was dissolved in isopropanol and subjected to filtration using a suction filter, there is a plausible risk of different amount of filtration due to a poor dissolving. The more likely risk, based on experience in the suction filtration, was the leaking of additional solids around the paper to the pre-treated IPA dissolved biocrude in case of failed suction and under pressure keeping the paper intact. This could result in an inaccurate or inconsistent representation of the feedstock. During the evaporation of isopropanol from the batch before the reaction, volatile components of the biocrude may co-evaporate, leading to a misrepresentation of the true composition of the biocrude. This is of particular concern as the HDO process depends on accurate pre-treatment of the biocrude. However, the processed biocrude was always compared to the batch and therefore differences between the produced batches should have an equal effect on the final results.

Post-reaction phase

After the HDO reaction, phase removal from the autoclave involves dissolving the oil and residual coke in ethyl acetate. Some biocrude components may not dissolve efficiently. The dissolution of the remaining biocrude and coke from the autoclave successfully transferred with the aid of solvent and it was unlikely that these would remain in the autoclave. However, it was noticed that the outside of the autoclave constantly had biocrude and catalyst, and water also poured from the autoclave around it to the bottom of the reactor. This meant that the original substances, including water, catalyst, and biocrude, had leaked to the bottom of the reactor and needed to be collected from the bottom of the reactor. A similar collection method was implemented in this case by using a bottle below the reactor to collect the water, and dissolving the remaining biocrude using ethyl acetate. Collecting samples from the bottom of the reactor below the autoclave proved to be difficult due to the bottom valve getting stuck with coked biocrude after each test, especially at higher temperature values. A screw under the autoclave was first opened. To collect the sample, a long sharp metal piece was used to force open the valve and allow the matter below the autoclave to fall out into the container. Unfortunately, this process resulted in the loss of some water, oil, and solid phases and took a considerable amount of time. The remains of the outside of the reactor were washed with ethyl acetate, but certain amount of the biocrude stayed on the surface around the autoclave.

Outliers due to complexity of biocrude

Biocrude is a complex matrix of numerous organic compounds and can behave unpredictable under certain conditions and cause experimental runs to deviate from the mean. The heterogeneity of the biocrude can also lead to inconsistencies when mixing with the catalyst. After the HDO reaction, the formation of a largely solid oil phase complicates the separation process. The subsequent dissolution of this oil and coke in ethyl acetate and their separation from solids such as coke and catalyst presents risks. There is potential for incomplete recovery or inconsistent separation, which could affect the purity and yield of the primary biocrude being investigated. The oil separated at the higher temperature was different and yielded less compared to the lower temperature end-product, raising the question of whether some of the oil was lost, converted to coke, evaporated or the combination of all the three together. The observed changes in yield could be attributed to chemical transformations occurring at higher temperatures. Variations in yield could also result for example from the decomposition or conversion of oil components into coke or gaseous compounds, impacting the overall quantity and quality of the oil recovered.

7.5.3 Experimental limitations

Control of variabilities

It is essential that the temperature, pressure and other conditions inside the reactor remain constant from one run to the next. While the time and temperature did not vary and remained close to the same or desired values, the nature of the process means that even minor fluctuations can introduce disparities in results. The leakage observed in the reactor is a significant limitation. The loss of the water phase during the procedure is one concern, but also the potential leakage of the oil can skew results considerably. The diminished biocrude yield observed at higher temperatures suggests that the increased pressure may worsen this leakage, leading to losses of biocrude as well. The gas phase dynamics within the reactor play an important role in the HDO process. In particular, the leakage in the reactor can also have an impact on the gas phase, particularly the potential loss of hydrogen. Hydrogen is critical to the hydrodeoxygenation process. A reduction in its availability in the reactor due to leakage could affect the efficiency of the HDO, resulting in unsuccessful deoxygenation and lower biocrude quality. The HDO process involves multiple steps, different solvents and equipment, and achieving consistent reproducibility across runs can be challenging. Variations in sample preparation, solvent interactions or instrument performance can lead to different results between experimental runs. A more detailed look to the variability of the process pressure conditions is taken below.

Analysis on Variability in Process Pressure Conditions

In the course of experimental runs, variations in the pressure conditions were observed, mainly due to a leakage due to a non-contact reactor. This chapter attempts to explain the impact of these variations on our results, with the aim of providing the reader with a transparent understanding of the data presented. During the experiments, significant pressure fluctuations were observed. This variability may cause the experiments to differ from the intended conditions. Our analysis suggests that the interplay of time, temperature, and initial pressure directly influences the magnitude of this leak-induced variation. A longer duration of the experiment could underline the leakage, while an elevated initial hydrogen pressure, by its magnitude, could accelerate the leak. In addition, higher temperatures increase the vapor pressures of the components in the reactor, especially water, making the system more susceptible to leakage similarly as increasing the initial hydrogen pressure.

The pressure change in measured from the initial reaction starting temperature to the end of the reaction at the same temperature. For example, if the pressure was 150 bars at the beginning of the reaction at temperature 315°C, and after 2 or 4 hours of reaction time, the pressure at the same temperature is 145 bars, the pressure change would be 5 bars. It is important to note that the pressure change would be naturally higher in tests conducted at higher temperatures, not only due to increased leakage, but also because of relative pressure. Therefore, they cannot be compared directly. The reason for measuring the reaction related pressure change was to minimize time-related leakage evaluation because the reaction condition pressure values are more important than, for example, the leakage during the heating or cooling phase. This provides a better overview of the reaction events. The pressure values also varied throughout the reaction. To better understand the overall reaction conditions, we calculated the average pressures. The data for the changes in the pressures are presented below in Table 25.

Table 25. Pressure variations and deviations observed during test runs.

ID	Process time (h)	Temp (°C)	Press, H_2 (bar)	Pressure Beginning (bar)	Pressure ending (bar)	Pressure change (bar)	Pressure min	Pressure max	Supercritical water (min)	Average pressure (bar)
69	3	320	30	164	162	**2**	162	172	-	**167**
70	3	320	30	160	157	**3**	157	174	-	**168**
71	3	320	30	152	148	**5**	148	166	-	**160**
72	2	320	15	104	132	**-28**	132	144	-	**123**
73	2	320	5	-	-	**-**	-	-	-	**No data**
74	2	380	5	192	195	**-3**	195	202	-	**199**
76	2	380	15	198	177	**21**	177	206	-	**193**
77	2	380	15	221	168	**53**	168	229	41	**209**
79	4	320	15	128	132	**-4**	132	142	-	**138**
80	4	320	5	119	113	**6**	113	126	-	**121**
81	4	380	15	222	69	**154**	69	232	20	**140**
84	3	350	10	159	158	**1**	158	175	-	**167**
85	2	380	5	201	206	**-5**	201	216	-	**210**
86	2	380	15	224	223	**1**	223	237	120	**232**
87	4	380	5	202	181	**22**	181	215	-	**202**
88	4	380	15	224	171	**53**	171	232	45	**202**
89	3	350	10	151	77	**74**	77	169	-	**89**

At a set temperature of 320°C, the pressure variability was relatively low, averaging around 3 bars but peaking at 28 bars. In the analysis of 17 experiments, tests conducted at 320°C exhibited minimal pressure variations, suggesting that reactions under these conditions are relatively stable. Conversely, at 380°C the pressure variability increased sharply, with an average leakage of 20 bars and a peak of up to 53 bars. Tests 81 and 89 resulted in a high-pressure change and a significantly reduced average pressure respectively and were therefore not considered suitable for average analysis.

One of the study's objectives was to investigate the influence of supercritical water on the reactions and their outcomes. Supercritical exhibits neither the properties of a conventional liquid nor those of a gas [140, 141]. After its boiling point, when the temperature and pressure of water exceed certain critical thresholds, it transitions into a supercritical fluid phase. These critical points are a temperature of 374.1 °C and a pressure of 220.6 bar. Given the relevance of these supercritical conditions, our experiments aimed to determine which tests approached or reached them, and for how long. Notably, a temperature of 380°C combined with particular starting pressures often resulted in pronounced pressure changes and enhanced the likelihood of reaching supercritical conditions. Only four tests at the 380°C managed to reach this critical point, with a single test maintaining these supercritical water conditions for its entire test duration, which makes the assessment of results difficult by introducing elements of inconsistency.

Ideally, pressure variations in the reaction setup should be minimal, if not zero. The resources needed to repair the equipment were not available. If the amount of total pressure change had been known earlier, the conditions could have been set more favorably in terms of leakage. For example, by studying the reaction at a lower temperature with a higher initial hydrogen pressure the pressure effect could have been studied more thoroughly. The elevated reaction temperature had an exponential impact on the total pressure, enabling the reaction to briefly reach supercritical conditions in some of the tests. These conditions were too much for the reactor to withhold the pressure. To maximize the usefulness of our experiments and to strengthen our data set, almost all tests were included in the analysis, despite their imperfections. By integrating both valid and unstable variable results, more comprehensive evaluation was ensured, providing more transparent insights for future experimental designs and potential experiments. The data is summarized in the following Table 26.

Table 26. Summary of Key Experimental Parameters and Observations from Pressure Fluctuation Tests.

Parameter	**Observations**
Pressure Fluctuations	Significant fluctuations observed. At 320°C, pressure changes ranged from 2 to 28 bars. At 380°C, they ranged from -5 to 53 bars, indicating both increases and decreases in pressure. Some tests, like Tests 81 and 89, showed particularly high fluctuations.
Temperature Impact	- 320°C: Low pressure variability, avg. ~3 bars, peak at 28 bars. - 380°C: Increased variability, avg. fluctuation of 20 bars, peak of 53 bars.
Pressure Role	Elevated initial hydrogen pressure could accelerate leak change. Higher temperatures and pressures increase susceptibility to leaks.
Supercritical Water	Four tests at 380°C reached this critical point. One test maintained these conditions throughout.

7.6 Safety evaluation

In the course of conducting hydrodeoxygenation (HDO) experiments with biocrude, safety was important due to the inherent risks associated with the process. The HDO process involves the use of a sulfided catalyst in the presence of hydrogen, and high temperature. This required safety protocols due to the potential generation of harmful molecules and the close contact with solvents. In recognition of the volatility and potential hazards of the chemicals involved, work was carried out under a fume hood.

During the sulfidation phase, which was mainly carried out in the early stages before the start of conditional testing, precautions had to be taken when handling chemicals such as dimethyl disulfide (DMDS) and hexane. Thick nitril gloves were used to prevent any direct contact and to ensure safety. It's worth noting that the sulfidation of DMDS, particularly in the presence of hydrogen, can produce harmful hydrogen sulfide which was a significant safety concern.

A fume hood was also placed over the reactor for potential gaseous product leaks during the HDO process. This setup provided ventilation and ensured containment of any potentially harmful fumes that might be generated during the process. It was observed that leakage in the reaction became more pronounced at higher temperatures. While these pressure fluctuations were relatively modest at lower temperature levels and shorter times, their increase at higher temperatures stressed the importance of preventing any access to the reactor chamber during operation. In addition, during the sulfidation of the catalyst, a change in pressure of around 2 bar at room temperature was noted after the reaction, which could mean a potential leak of hydrogen sulfide.

The reactor can reach a temperature over 400°C and withstand pressures of up to 250 bars. To minimize risks, the reactor was located in a separate room. The ongoing reaction conditions - temperature, pressure, and duration - were monitored remotely from a computer. A moveable obstacle was set to seal the room, which was marked to indicate about the ongoing reaction, preventing anyone from approaching the reactor. These precautions were necessary due to the potential dangers of equipment malfunction and pressure leakages during the reaction. Ventilation was also crucial due to concerns about volatile substances formed during the reaction. The room was given sufficient time to ventilate before accessing it without a gas mask. To ensure safety it was imperative that the reactor room remained inaccessible.

Given the risks associated with the potential release of harmful gases such as hydrogen sulfide during the sulfidation of DMDS and the potential formation of unknown substances during the heating of the biocrude solution, a gas mask was an essential piece of safety equipment. It was initially used when transferring samples from the fume cupboard to the reactor and when cleaning the reactor after the reaction but was also used when handling samples in the fume cupboard after the reaction. The strong odor of the biocrude signaled the potential presence of hazardous compounds, making the use of a gas mask necessary during both sample transfer and subsequent filtration processes, even when handled under a fume hood, to ensure protection from any residual vapors or volatile compounds.

8 Conclusion

The pre-treatment process applied to pine biocrude showed improvements in its elemental composition. Filtration yields varied between 67% and 87%, possibly influenced by the heterogeneous nature of the biocrude and the filtration parameters. In particular, there was a reduction in oxygen content, from an initial 29.8% to a range of 21.5% to 26%. At the same time, both carbon and hydrogen levels increased, emphasizing the removal or reduction of undesirable constituents during pre-treatment. Pre-treatment improved the quality of the biofuel, as evidenced by the increased hydrogen to carbon (H/C) ratio and improved higher heating value (HHV) - from an initial 27.8 MJ/kg to an average of 31.21 MJ/kg across the batches. Even before the introduction of HDO experiments, pre-treatment alone improved the intrinsic properties of the biocrude. It increased both the carbon and hydrogen content while reducing the oxygen concentration. This underlines the promise and potential of refining pre-treatment processes in biofuel production.

Catalysts were compared and selected based on Ranido's own performance test, which had indicated good catalyst stability along with the literature review. All three catalysts were tested individually via HDO. The yield of upgraded biocrude varied quite significantly due to sample recovery problems in the first test, but other biocrude characteristics were quite similar. Considering all three catalysts, the average DOD achieved was approximately 6%. This showed modest deoxygenation, with distinguishable variations between the catalysts. The average carbon content across the catalysts was around 69.2% and the hydrogen content was around 8.37%. The average HHV across 3 catalyst experiments was approximately 31.73 MJ/kg. The test with unsulfided Ru/AC had slightly more favorable deoxygenation, elemental composition and energy content. The changes between sulfided Ni/Mo were minor. The test with sulfided Ru/AC was unsuccessful and differed on its after-treating principle so a straightforward conclusion cannot be made between all the catalysts.

The hydrodeoxygenation (HDO) process of pine biocrude under varying conditions of temperature, pressure and time were performed using a sulfided Ru/AC catalyst. Temperature was the most impactful parameter influencing the yield and HDO outcome. Higher temperatures slightly decreased the carbon and hydrogen content of the biocrude. Elevated temperatures didn't promote deoxygenation or improve the heating value of the biocrude, on the contrary, they had a slightly negative effect on it. Overall, the effect of conditions on elemental composition and deoxygenation was minimal in the HDO experiments and there was no clear indication of a specific factorial combination for improved results. The yield exhibited correlation to the temperature conditions, and there was a trend for decreased biocrude yield with increased reaction temperature. The excessively high temperatures may have had undesirable effects, increasing gas and coke formation, which leads to a reduced overall yield of the upgraded biocrude.

The complex relationship between pressure and temperature became apparent, highlighting the need for understanding of their combined influence on the HDO process. It became clear that a linear correlation may not exist in all areas. The pressure values based on the pressure variability analysis, exploited the fact that there were major differences in the actual pressure values during the reaction, very likely due to the pressure leakage. The hydrogen load between 5 and 15 bars, is quite low in itself, and therefore the difference between pressure values did not have as distinguishable effect on the reaction outcome as the temperature.

Time did have some influence, but it did not always have a direct relationship with the in yield or deoxygenation. Even though the reactions usually progress over time, any continuous time-dependent leakage during the experiment can lead to losses of biocrude, water and gas, which in turn can affect the overall yield. The time variable would likely become more apparent in an experiment with more profound changes in the biocrude. Due to small changes in the composition, the impact of time is hard to notice as well.

The best conditions for upgraded biocrude yield, both in terms of mass and carbon balance, were generally with lower temperature range. More specifically at a temperature of 320°C, a pressure of 5 bars and 4 hours of with average yields of around 55% for mass and carbon balances. The best conditions for deoxygenation were obtained at 320°C, 5 bar pressure and 2 hours reaction time with a DOD of 10%. The conditions giving the highest heating value (HHV) were 380°C, 5 bar H_2 pressure and 2 hours reaction time, resulting in an HHV of 32.6 MJ/kg.

In conclusion, this research has provided a comprehensive analysis of the HDO process of pine biocrude using a sulfided Ru/AC catalyst, highlighting the roles of temperature, pressure and time. The results provide insights to optimization of the reactor conditions with the objective of maximizing yield and improving fuel quality. The HDO experiment failed to produce desired results in lowering the biocrude oxygen levels to the desired levels. The conditions did affect the outcome of the upgraded biocrude, and the data could be used for setting the conditions for biocrude in the future to maximize either yield or deoxygenation of the biocrude, although the performed HDO experiments cannot be addressed effective in terms of deoxygenation. The quality of the biocrude has a significant impact on the results of the work and points out the importance of the biocrudes characteristics for processing efficiency. High viscosity biocrude, together with elevated oxygen levels, complicates processing and requires further solutions to improve conversion, yield and high oxygen content.

To further improve the HDO process, lowering the temperature range to maximize biocrude yield may be essential and would likely favor the thermal stability of the catalyst in the reaction and avoid coking. With the current reactor and pressure limitations, by lowering the temperature range, the hydrogen pressure load could be increased. By increasing the hydrogen load, the reaction could lead to more successful deoxygenation pathways, facilitating more oxygen removal and increasing the hydrocarbon content of the biocrude. As deoxygenation did not occur in the HDO experiments, this could be the proposed approach for future experiments with biocrudes.

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