

Master's Programme in Biological and Chemical Engineering for a Sustainable Bioeconomy

The Development of Sustainable Aviation Fuels from Lignin Fragments

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Abstract

Sustainable Aviation Fuel (SAF) is considered a high-potential solution for the decarbonization of our energy systems, and is under development in many countries of the world (International Air Transport Association, 2022). However, the seven current certified SAF production technologies are unable to fulfill the requirements of aromatic compounds, necessitating a maximum blend proportion of 50 vol% with fossil-based aviation fuels (Cheng and Brewer, 2017, ICAO).

Lignin, a major component of lignocellulosic biomass constituting 20-30% of wood resources, is the largest renewable source of aromatics (Tuck et al, 2012). Although typically regarded as a waste stream, lignin valorization is forecasted to improve the economics, sustainability, and circularity of a biorefinery concept, and due to its abundance and aromaticity, constitutes significant potential for industrial use in the replacement of oil-based products (Abu-Omar et al, 2021, Stone et al, 2022). Lignin fragments (LHD) following a proprietary process are composed of monomeric and dimeric fractions and possess a carbon range similar to those found in SAF mixtures.

In this work, a hydrodeoxygenation (HDO) reaction was designed and optimized to produce SAF-range hydrocarbon from LHD. Various reaction conditions were manipulated in order to understand the internal reaction kinetics and tune reaction conditions for the desired products, according to whether aromatic components are desired or full saturation products. It was found that the ratio of hydrogen to oxygen ratio has the most significant influence in the product selectivity, followed by the reaction temperature. An increase in the ratio of hydrogen to oxygen content decreased the proportion of aromatic compounds in favour of saturated species, although a minimum molar ratio was required for complete HDO; therefore this minimum ratio is optimal for aromatics production, whereas a higher ratio is optimal for the production of cycloparaffins while minimizing excess hydrogen use and further undesirable reactions such as cracking. An increase in the reaction temperature favours the production of aromatics and favours the HDO reaction while inhibiting the ring hydrogenation reaction. However, the oil yield also decreases with temperature, due to an increased rate of C-C cleavage (i.e., cracking). It was also observed that an increase in reaction duration at a constant temperature led to a decrease in the aromatic fraction, with a very slight decrease in oil yield. This suggests that the ring hydrogenation reaction continues to hydrogenate aromatic species following HDO, and that C-C cleavage is unfavoured. In contrast, at higher temperatures, where the ring hydrogenation reaction is less favoured, increased reaction time does not lead to a decrease in aromaticity, but to decreases in oil yield. This process was found to successfully deoxygenate lignin fragments to produce SAF-range hydrocarbons with a tunable aromatics content, that could be used as a SAF or blended with other SAF pathways in order to provide a 100% fossil-free aviation fuel.

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Preface

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List of Abbreviations

AAF: Aldehyde Assisted Fractionation

ECN: Effective Carbon Number

G: Guaiacyl lignin structure

H: Hydroxyphenyl lignin structure

HDO: Hydrodeoxygenation

LHD: Lignin Heavy Distillates

RCF: Reductive Catalytic Fractionation

S: Syringyl lignin structure

SAF: Sustainable Aviation Fuel

1. Introduction

1.1. Context

In the ongoing attempt to slow the effects of climate change and limit the rise in global temperatures to under 2°C, up to 70% of our current greenhouse gas emissions must be eliminated by 2050. (Gao et al, 2017). To this end, worldwide efforts are being developed to decarbonise our energy systems, notably through the generation of renewable electricity and the electrification of personal transportation vehicles. However, in applications deemed “hard to abate sectors” such as aviation, liquid fuels remain necessary due to the physical specifications requiring a compact, high energy density carrier (Liebetrau et al, 2021). Existing commercial aviation fuels adhere to the strict performance requirements of aviation fuel, however they are fossil-based and carbon intensive; in order to reduce the environmental impact of this sector, the development of Sustainable Aviation Fuels (SAFs) is of global interest (US Department of Energy, 2022, European Parliamentary Research Services, 2022, Yirui et al, 2022). SAFs are fuels derived from non-fossil sources, and can be made from widely available domestic feedstocks with multiple established technical pathways to their generation (International Air Transport Association, 2022). The first test flight using biojet fuel was performed in 2008, and over the following 15 years, 450,000 flights have been executed using SAFs (International Air Transport Association, 2022). However, regulation surrounding eligible biofuel substrates differs by country; for example, German biofuels utilize energy crops such as maize as their dominant feedstock, whereas other countries such as Switzerland oppose the use of dedicated energy crops due to competition with food resources (Liebetrau et al, 2021). In order to create SAF that could truly be considered sustainable, it must not constitute direct or indirect competition with agricultural activities or cause indirect land use change (ILUC) that may cause the release of CO₂ currently stored in trees and soils, which counteracts the greenhouse gas reductions from the use of biofuels (European Union RED II, 2018). As such, one promising raw material for sustainable fuel generation is non-food lignocellulosic biomass, such as wood or agricultural residues.

There are seven currently certified SAF production pathways, which utilise mainly fatty acid, sugar, or alcohol feedstocks (International Air Transport Association, 2022). To achieve SAF production on a large enough scale to readily meet aviation demands, a sufficiently high-volume process is needed. The fuel mixture produced must be composed of linear and branched aliphatic components as well as aromatic and cycloalkane species in order to be compatible with many existing turbine engines (Stone et al, 2022). Although the cycloalkanes and aromatics components comprise between 30 to 70 wt% of aviation fuels mixtures, current certified SAF production technologies are unable to fulfil the required composition as their feedstocks do not include sources of these aromatic structures (Stone et al, 2022, International Air transport Association, 2022). Because of this, current SAFs are blended with conventional fossil-based aviation fuels at a maximum proportion of 50 vol%. This blend achieves a minimum of 8 vol% of aromatics (Cheng and Brewer, 2017). Although newly produced turbine engines no longer require aromaticity, many existing aircraft require this fraction; due to the long turnover time estimated at a minimum of 14 years for the replacement of a fleet of aircraft, it is desirable to produce a SAF that contains these aromatic structures that many existing aircraft still require in order for prompt decarbonization of the aviation sector (Hileman & Stratton, 2014). In order to achieve a 100% drop-in SAF without fossil fuel blending, the generation of these elusive cycloalkane and aromatic components must be achieved, and the technology must be capable of producing large volumes from abundant and sustainable feedstocks.

Lignin, a major component of lignocellulosic biomass constituting 20-30% of wood resources, is the largest renewable source of aromatics (Tuck et al, 2012). As a common by-product of cellulose-focused industries such as papermaking, lignin is isolated on a large scale and typically regarded as a waste stream, often simply burned to recover heat (Koranyi, 2020, Bertella and Luterbacher, 2020) However, recent techno-economic analyses and life-cycle assessments suggest that lignin valorization would improve both the economics, sustainability, and circularity of a biorefinery concept (Abu-Omar et al, 2021, Luo et al, 2022). The chemical complexity and abundance of lignin, due to the presence of aromatic structures conventionally found in oil, constitutes

significant potential for industrial use in the replacement of oil-based products (Stone et al, 2022).

1.2. Background

Lignin is the second most abundant biopolymer in the world after only cellulose, with an estimated 50 million tons in production annually (Demuner et al, 2019). Lignin comprises 15-30% of plant biomass, and serves within a plant to assist structure by providing adhesion between cellulose fibers, and control plant moisture content by establishing the water barrier of plant fibers due to its hydrophobicity (Ek et al, 2009, Lourenco and Pereira, 2017). Lignin is a polyphenol composed of three phenolic monomers: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol exhibiting the structures hydroxyphenol (H), guiacyl (G), and syringyl (S), displayed in Figure 1 (Ek et al, 2009, Abu-Omar et al, 2021).

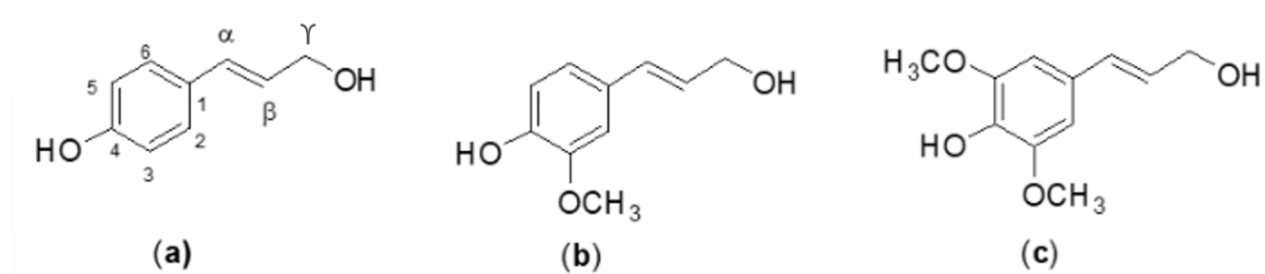


Figure 1. Structures of hydroxyphenyl (a), guiacyl (b), and syringyl (c) lignin monomers (Demuner et al, 2019)

As displayed in Figure 1, the monomers differ by the number of methoxy groups attached to their ring: S has two methoxy groups, G has one, and H has no methoxy groups. This contributes to the diversity of intermonomer bonds, with less-substituted monomers capable of forming more crosslinking in the supramolecular structure. Their distribution is dependent on the type of plant: softwood lignin contains almost exclusively G with small amounts of H, while hardwood lignin contains both S and G in ratios varying from 1.2 to 3.0, and grass lignin contains all three monomers. (Lorenco et Pereira, 2018,

Balakshin et al, 2016) Although many bond types can exist between monolignols, the most common is β -O-4 aryl ether bond. However, the carbon-carbon bonds between monolignols, most common in the case of G lignins, are more resistant than the ether bonds, and are more likely to survive through harsh chemical treatments (Ek et al, 2009, Demuner et al, 2019). There are many possible functional groups within the lignin polymer including both phenolic and aliphatic hydroxyl, methoxyl, carboxyl, carbonyl, and benzyl alcohol, each with different reactivity which can vary between lignin types (Ek et al, 2009, Demuner et al, 2019). In plants, the monolignols are polymerised via radical polymerization and are arranged in a three-dimensional web by a random order of various ether or carbon-carbon bonds as shown in Figure 2 (Ek et al, 2009, Abu-Omar et al, 2021).

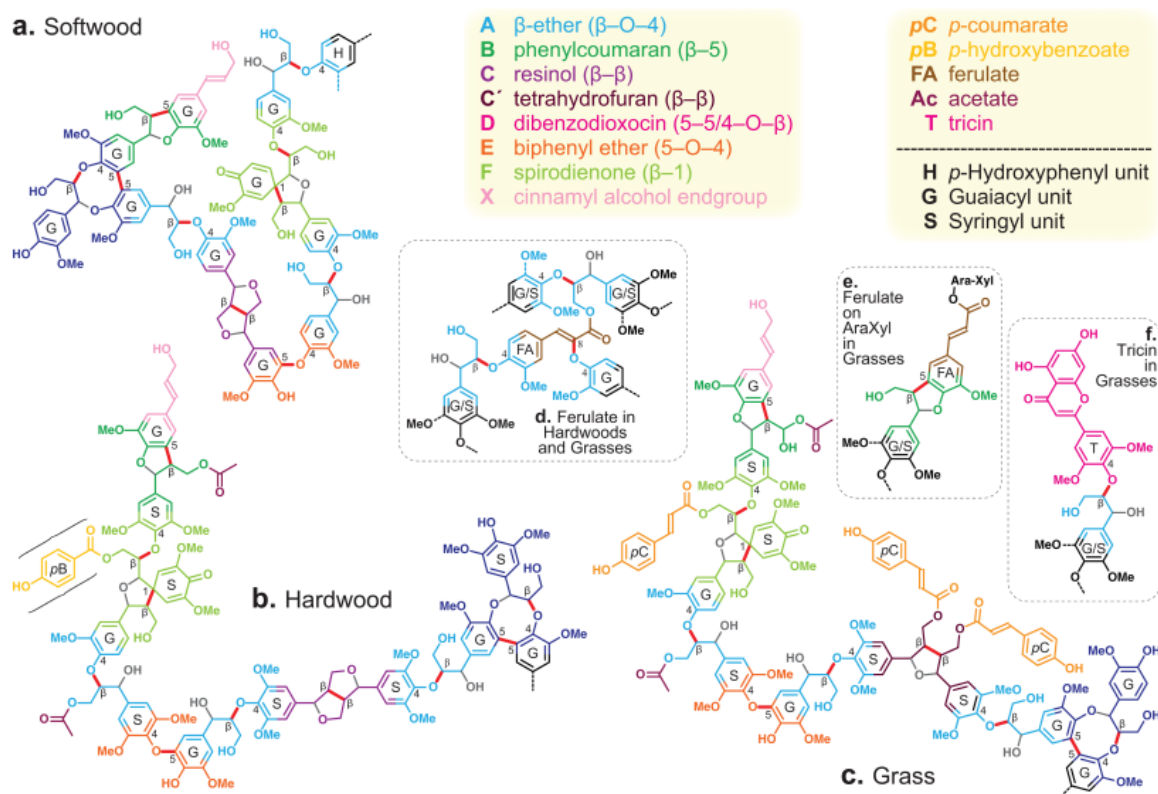


Figure 2. Schematic of lignin's polymeric structure indicating possible lignin units and connections. Adapted from Abu-Omer et al (2021)

It is increasingly being shown that lignin in its native state is less recalcitrant than previously believed, as evidence suggests that natural lignin structures are modified during lignin processing and isolation (Luo et al, 2022, Ek et al, 2009). Nevertheless,

lignin remains a complex polymer that is as of yet not fully characterized and understood (Lourenco and Pereira, 2017).

Due to the abundance of lignin and its generation as a byproduct of cellulose-based industries, there is an increasing number of products being developed using lignin in various applications. One increasingly common application of lignin streams is as dispersants in the form of lignosulfonates, or as activated carbon adsorbents and filtration systems (Demuner et al, 2019). Another high-potential application is as carbon fibers for the generation of composite materials for purposes such as the automotive industry, as a biologically-sourced and abundant alternative to costly polyacetylonitrile (Demuner et al, 2019). Other potential high-value products can result from the depolymerization of lignin; notably, vanillin is a food additive that is typically produced from petrochemical sources, however lignin could be a viable and economically feasible feedstock for this high added-value product (Pacek et al, 2013). In light of the possible transformations which lignin can undergo, different streams and fragments can concurrently be utilized for multiple applications, enhancing the economic viability of biorefinery schemes through efficient use of the biomass raw material (Liao et al, 2020). Lignin and its fragments have also found potential applications in the replacement of common plastics and chemicals, with the benefit of its demonstrated antioxidant activity (Ponnusamy et al, 2018). Due to the importance of aromatic compounds in sectors such as fragrances, coatings, and resins, attention is being given to the potential of lignin as a renewable feedstock in these areas as well (Bertella and Luterbacher, 2020, Luo et al, 2022). Figure 3 displays a visual overview of some of the chemical pathways by which different components of lignin can be upgraded, corresponding to their potential applications.

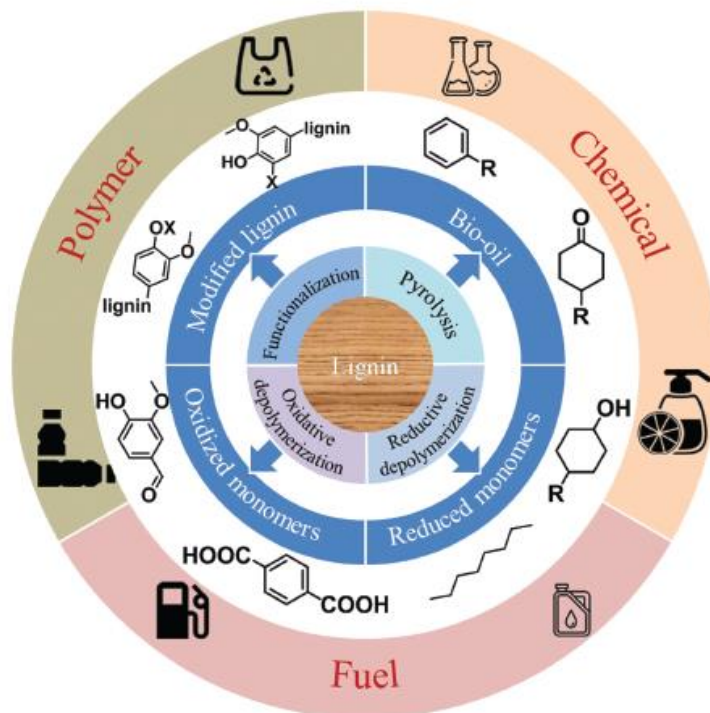


Figure 3. Diagram of potential upgrading pathways for lignin and resulting molecules, with corresponding fields of application (Wong et al, 2020).

In order to separate lignin from cellulose and hemicellulose for further processing, various fractionation techniques have been employed. The most traditional and widespread of these is the kraft process of the papermaking industry, where lignin is solubilized in a highly alkaline environment of NaOH and Na₂S at temperatures between 155°C and 175°C, ionizing the phenolic groups which then react with the bisulfide ions to hydrolyse β-aryl ether bonds as shown in Figure 4 (Demuner et al, 2019).

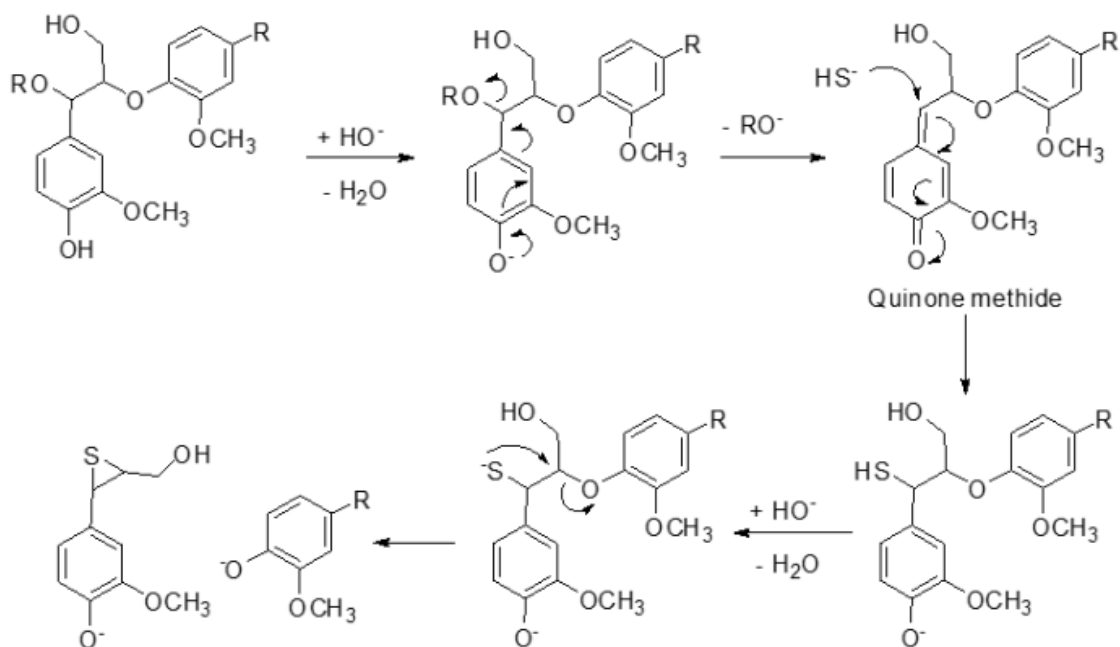


Figure 4. Schematic illustration of the kraft pulping process leading to the hydrolysis of β -O-4 linkages (Demuner et al, 2019)

This process separates the lignin from the other plant components, however these separation techniques typically lead to increase recalcitrance of lignin making valorisation difficult (Luo et al, 2022). This is due to condensation reactions of the lignin in these highly severe alkaline conditions; the proportion of aliphatic hydroxyl groups and b-O-4 groups are reduced, and the proportion of phenolic hydroxyl groups, carboxylic acid, and carbonyl groups are increased, promoting the formation of condensed structures (Demuner et al, 2019). Following the kraft process, the lignin can be precipitated by acidification of the highly alkaline solution, however the challenges with the isolation of lignin due to its complex structure and heterogeneity as well as low solubility make burning for energy recovery the most common use of kraft lignin (Demuner et al, 2019).

Subsequently developed methods for improved lignin extraction are organosolv processes. These processes use an organic solvent, usually methanol or ethanol, to isolate lignin from biomass, often with an acid catalyst and water. The lignin is then precipitated, and the solvent can be recovered (Torres et al, 2020). The organosolv process is advantageous compared to the Kraft process due to improved yield and purity of lignin

recovery, with little to no sulfur content of the resulting lignin (Cheng and Brewer, 2017). However, in these acidic conditions, ether and ester bonds are cleaved, and the γ -OH lignin structure is protonated, leading to the formation of benzylic carbocations, as shown in Figure 5 (Abu-Omar et al, 2021).

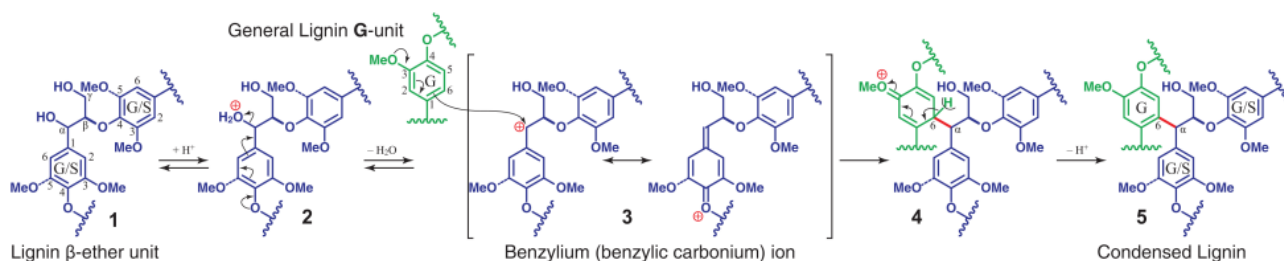


Figure 5. Schematic showing the condensation of G lignin via the formation of benzylic carbonium under acidic conditions (Abu-Omar et al, 2021)

These structures, by electrophilic aromatic substitution with the aryl groups of lignin, form new C-C bonds within the lignin chain which do not exist in native lignin and are very recalcitrant, and can not be depolymerized for subsequent applications (Abu-Omar et al, 2021). These condensation reactions occur under harsh acidic and alkaline conditions, as well as during thermochemical pre-treatments such as steam explosion due to the release of native acids from esters found in the plant cell wall, and each of these methods yield low-quality lignin as a result. (Abu-Omar et al, 2021).

Alternative fractionation techniques that favour the elaboration of lignin-based products promote a so-called “lignin first biorefinery”; These techniques ensure stabilisation of lignin during separation processes of the biomass to obtain isolated lignin without undesirable condensation reactions, in order to valorise both lignin and polysaccharide fractions (Abu-Omar et al, 2021). The first developed of these is Reductive Catalytic Fractionation (RCF), in which lignin is extracted from biomass with the aid of a solvent in the presence of a transition metal catalyst and a hydrogen source. At high temperatures, solvolysis, hydrogenation, and hydrogenolysis reactions occur in order to cleave ester and ether bonds within the biomass structure and the lignin polymer (Liao et al, 2020). The catalyst serves to stabilize the reactive intermediates resulting from the solvolysis of lignin, and the solvent determines the degree of extraction of lignin as well as its purity. (Liao et al, 2020, Abu-Omar et al, 2021). This process yields a carbohydrate

pulp, which is suitable for the variety of existing cellulose valorization processes, and a lignin oil with near-theoretical yields of phenolic monomers (Liao et al, 2020). More recently Aldehyde Assisted Fractionation (AAF) has been developed, which uses a diol functional group present in lignin side chains to form an acetal with an aldehyde and cap the benzylic alcohol. This prevents the formation of a benzylic cation, therefore avoiding lignin condensation and stabilizing the lignin to allow for transformations (Abu-Omar et al, 2021). Formaldehyde was successfully employed by Shuai et al (2016) to protect the lignin structure during fractionation, giving monomer yields of 47 mol% compared to 7 mol% in the case of extracted and partially condensed lignin. There were two routes by which the formaldehyde hindered the formation of new C-C linkages in lignin; by the formation of a stable 1,3-dioxane structure with the 1,3-diols on the lignin side chains, and by the electrophilic aromatic substitution of protonated formaldehyde with the ortho or para positions of the aromatic ring to form hydroxy-methyl groups that blocked these reactive positions. This is illustrated in Figure 6:

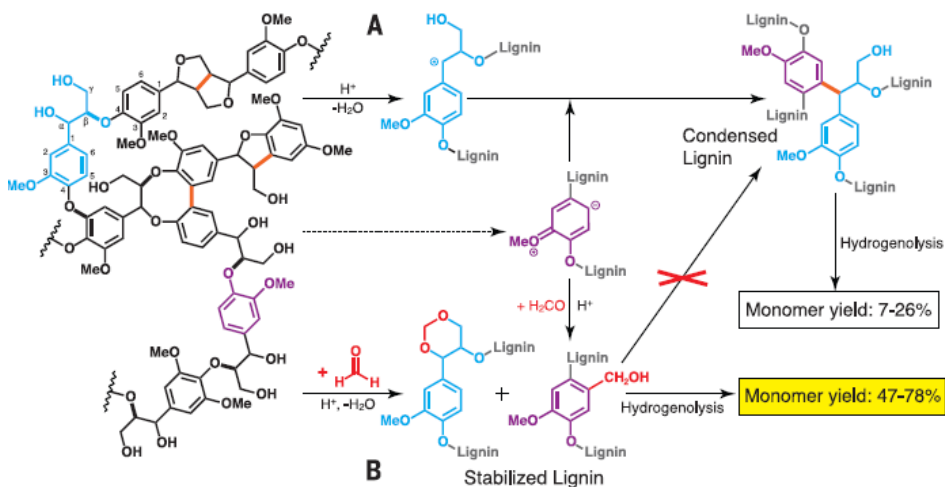


Figure 6. Diagram of lignin monomer production in A) an acidic, non-protected process and B) a formaldehyde-stabilized process (Shuai et al, 2016).

These results using formaldehyde suggest that lignin could be much more easily valorized concurrently with other biorefinery platforms due to the protection of the aldehyde (Shuai et al, 2016). However, due to the toxicity of formaldehyde, the suitability of other similar aldehydes has been evaluated (Lan et al, 2018). Acetone and butanone were tested and displayed some moderate protective effect on lignin extraction and improvement of

monomer yields after hydrogenolysis, but the greatest impacts were seen in the case of acetaldehyde and propionaldehyde, giving monomer yields (37 and 42 wt%, respectively) comparable to the 47% yield obtained with formaldehyde. Due to the protection of the lignin against the formation of unwanted C-C linkages, AAF lignin can be considered a strong starting material for a variety of high-value materials as part of a biorefinery scheme, including aromatics moieties.

Both RCF and AAF are known to produce near-theoretical lignin monomers, which present an attractive opportunity to synthesize saturated species and aromatics. Given the oxygen content of these lignin monomers, well above that allowable for SAF applications, a subsequent refining step such as hydrodeoxygenation (HDO) could be performed with the lignin stream following fractionation to remove oxygenated species under a hydrogen environment at temperatures of 300-450°C (Stone et al, 2022, Cheng and Brewer, 2017). These HDO reactions produce stable aromatic hydrocarbons and alkyl-cycloalkanes by breaking C-O bonds and saturating C=C bonds, while oxygen is removed in the form of water (Cheng and Brewer, 2017). The reaction is commonly done with an acid/redox-metal catalyst, but not all of these catalyst systems can selectively deoxygenate lignin monomers while preserving the aromatic structure. Often, catalysts that show promise in theoretical modelling exhibit low deoxygenation efficiency with real lignin feedstocks. This is mainly due to the recalcitrance of lignin, which necessitates complex reaction engineering, implies fast deactivation by coking, and an excessive hydrogen consumption from side reactions such as hydrocracking to form gaseous products (Stone et al, 2022). A theoretical modelling of a phenolic mixture with a Mo₂C catalyst showed that deoxygenation starts at 150°C, and that 280°C was sufficient temperature for complete deoxygenation (Lee et al, 2014, Chen et al, 2016). In contrast, the HDO of RCF lignin oil with the same Mo₂C catalyst system for the production of SAF-range aromatic compounds found that a temperature of 350°C was required to achieve stable deoxygenated compounds (Stone et al 2022). This study proposed a two-pass operation with an initial pass at 350°C followed by 375°C to maximize yields of SAF grade products. This two-phase process was necessitated as in a single pass, temperatures exceeding 350°C showed increasing loss of monomers and dimers through condensation reactions, while lower temperatures exhibited increased catalyst deactivation and less effective deoxygenation

(Stone et al, 2022). It has been theorized by Cheng and Brewer (2017) that there are two main reactions occurring during the HDO: direct HDO, where the C-O bonds in side chains are cleaved but the aromatic character of the molecules remain, and hydrogenation, where the aromatic ring is first saturated followed by the hydrogenolysis of the C-O bonds, generating a cycloalkane product. These mechanisms and their potential routes are shown using the example of the molecule guaiacol in Figure 7.

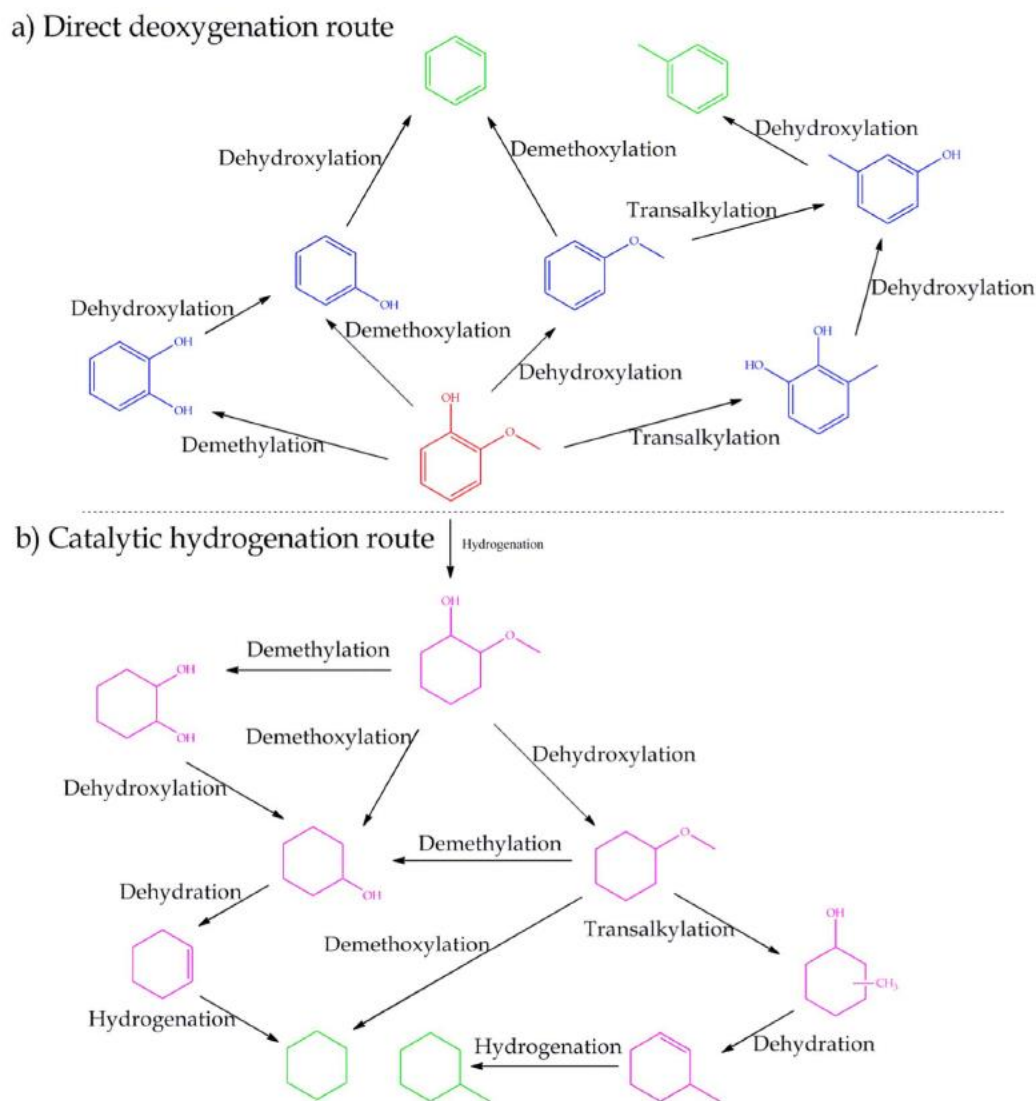


Figure 7. Proposed HDO mechanism showing two possible reaction routes (Cheng and Brewer, 2017)

The predominant reaction pathway and the final product distribution are highly influenced by the temperature and the nature of the chosen catalyst (Cheng and Brewer, 2017). Pt, Rh, Pd, and Ru have all been shown to exhibit high hydrogenolysis activity

(Héroguel et al, 2019). While catalysts are able to selectively impact activation energies of the various functionalities in lignin fragments, the reaction temperature could affect the kinetics of the desired reactions. In a study of the kinetics of the hydrogenation and HDO reactions, the adsorption of the reactants on the catalyst was found a key factor in determining the reaction rates, and thus the favoured reaction pathway (Massoth et al, 2006). It has also been seen that the preservation of aromaticity is favorable at higher reaction temperatures, while the ring saturation happens preferentially at lower temperatures below 340°C (Maki-Arvela & Murzin, 2017). However, high reaction temperatures to preserve aromaticity could also lead to degradation of non-fully deoxygenated species.

There have been many documented examples of discrepancies between Ru-catalyzed HDO results with lignin model compounds and with real depolymerized lignin (Stone et al, 2022, Héroguel et al, 2019). One likely reason for this is the difficulty in isolating lignin in a form suitable to the conditions of HDO, which typically takes place either in the gas phase or in the liquid phase using apolar solvents or neutral-pH water, of which lignin is typically soluble in neither. In addition, the HDO reaction is negatively affected by the presence of impurities such as other biomass components, therefore the lignin must be both relatively pure and uncondensed. These constraints have limited studies on lignin HDO in the past, however with the development of lignin-first biorefinery strategies such as AAF to isolate lignin while preventing condensation, lignin HDO could potentially produce results closer to those achieved with model compounds (Héroguel et al, 2019).

Both aqueous and organic solvents have been shown to successfully serve as hydrogen donors for HDO reactions (Cheng and Brewer, 2017), and a solvent-free process under a gaseous hydrogen atmosphere has been successfully demonstrated by Stone et al (2022), which significantly improves green chemistry metrics such as atom economy; this process also gave significantly improved carbon yield compared to previous processes (Wong et al, 2020) and 64% of products were in a suitable range for SAF use. As determined by a standardized fuel testing method, physical properties were near or improved from conventional fuel aromatics, including lower surface tension and freezing

point, and higher lower heating value (LHV) than traditional Jet A (Stone et al, 2022). While physical properties of the hydrodeoxygenated lignin oil conformed to ASTM standards, residual oxygen concentration remained at 2.1%, well exceeding the ASTM defined limit of 0.5% (Stone et al, 2022). In order to obtain a conforming lignin-derived SAF additive, improved deoxygenation must be developed. Baldauf et al (1994) found that harsher reaction conditions could increase oxygen removal to 99.9%, however, taking into account the drawback of higher-temperature reactions as described by Stone et al, measures must be taken to achieve this increase in deoxygenation without promoting condensation reactions that lower the yield of useful products. In addition, in order to develop a fully lignin-derived SAF, other paraffinic compounds are desired, such as cycloalkanes and isoalkanes, potentially requiring other hydrogenation, ring opening, and hydrocracking reactions (Stone et al, 2022). Due to variation in aviation turbine requirements, coupled with the long turnover time estimated at 14 years to replace existing aircraft to standardize or accommodate changes in fuel characteristics (Hileman & Stratton, 2014), the control over aromatic fractions in SAF composition could be desired.

1.3. Objectives

In this work, a hydrodeoxygenation process is designed and optimized to produce aviation grade fuels from a lignin fragment stream (LHD). To do so, three objectives are explored:

1. The effect of hydrogen-to-oxygen ratio on product distribution to develop a tunable product distribution profile and ensure deep deoxygenation compliant with ASTM SAF standards.
2. The effect of reaction parameters including temperature and time on product distribution in the context of avoiding unnecessarily harsh conditions and undesirable side-reactions
3. The effect of catalyst amount on product distribution and deoxygenation extent.

The development of this refining process will serve as proof-of-concept for the development of SAF from this lignin type, with a tunable product distribution in response to variable aromatic fraction requirements. The creation of a fuel mixture containing a full array of desired components from this abundant and renewable feedstock could serve as a drop-in fuel to higher blending ranges and enable the decarbonisation of the aviation sector.

2. Experimental

2.1. Chemicals and Materials

All chemicals were analytic reagents grade, and were used without further purification. The catalyst used was a bulk nickel and nickel monoxide catalyst. The chemicals used were dodecane (>95%) purchased from Fischer Chemicals, and absolute ethanol (EtOH) purchased from VWR Chemicals. Nitrogen (99.999%) and Hydrogen (99.999%) were purchased from Messer.

A 75mL Parr (Series 4740) reactor was used with a maximum nominal pressure of 551 bar and maximum temperature of 500°C, equipped with a pressure gauge rated for up to 800 bar and a 0.25 in A3039-71-XXX rupture disc rated for 400 bar. The reactor setup is shown in Figure 8. The pipes, valves and fittings used to create the reactor setup were purchased from Swagelok. Heat to the reactor was supplied by a 700W Parr ceramic fiber heating mantle, and a Heidolph MR Hei-tec plate and magnetic stirrer. A custom temperature controller and K-type thermocouples were purchased from Omega.

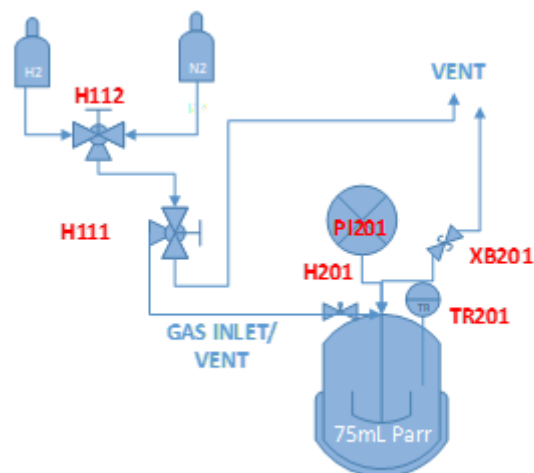


Figure 8. Reactor setup including reactor, pressure gauge P201, 3-way ball valves H111 and H112, 2-way needle valve H201, rupture disk vent XB201, and K-type thermocouple TR201.

A Heraeus Megafuge 1.0 centrifuge was used. For characterization, a Gas Chromatographer – Flame Ionization Detector (GC-FID) installed with a HP-5 column

(Agilent, 19091J-314) was used. 1.5 mL vials used for GC analysis were purchased from Infochroma AG. 0.45µm PTFE syringe filters from Cobetter Filtration Equipment Co. were used for filtration.

2.2. Feedstock: LHD

The LHD feedstock is a downstream product from a proprietary lignin depolymerization and upgrading process. The composition of the LHD sample was investigated by Elemental Analysis (Figure 10b) and GC-MS (Figure 10c) using silylation as derivatization method. In order to execute this procedure, the LHD sample was prepared for derivatization by dissolution in dioxane to make a ca. 10 mg mL⁻¹ solution. Upon filtration using a 0.22µm PTFE filter, 600 µL of the 10 mg mL⁻¹ LHD solution was added into a 2 mL GC-vial followed by 50 µL of pyridine and 100 µL of the silylating agent (N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (Sigma Aldrich)). The solution was then heated for 20 min at 50°C before being injected on the GC-MS for characterization.

2.3. Experimental Procedure

The transformation of LHD into fuel grade stream was performed by HDO. The LHD was first mildly heated (ca. 35-40°C) with an Einhell TE HA-2000E heat gun for 1-2 minutes to lower the viscosity and allow for flow of the material. 5 to 7 g of the LHD was poured into the Parr reactor, depending on the desired hydrogen-to-oxygen molar ratio (H₂:O). The H₂:O molar ratio was calculated following Eq. 1. The amount of H₂ (mol) were calculated using the Van der Waals equation of state (Eq. 2, Hoover et al, 1975) and the oxygen moles were calculated using the loaded mass of LHD into the reactor and the oxygen concentration found in the elemental analysis shown in Figure 10.

$$H_2:O = \frac{n_{H_2}}{n_O} \quad \text{Eq. 1}$$

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad \text{Eq. 2}$$

Where n is the amount of H_2 , V is the gas volume in the Parr reactor, assumed to be equal to the volume of the reactor minus the solution volume ($\sim 70\text{mL}$), T is the temperature of the H_2 while loading, p is the initial pressure of the H_2 loaded into the reactor, R (8.314 J/molK) is the universal gas constant, and a and b are constants of $0.245 \text{ L}^2/\text{mol}^2$ and 0.0265 L/mol , respectively, for a hydrogen system found in literature (Engineering Toolbox, 2017).

The desired amount of catalyst was weighed and added to the reactor after the LHD. A 2cm magnetic stir bar was placed inside the reactor. The reactor head was screwed onto the reactor, and the securing bolts were tightened with a $5/16''$ Allen key to seal the reactor. The reactor was then connected to high pressure flexible tubing with a 16 wrench, purged twice with 10 bar N_2 , and once with 50 bar H_2 . The reactor was then pressurized at the desired pressure, left for 5 minutes for leak check. The reaction temperature was set to the desired temperature with an alarm setting of 10°C above the set temperature. The stirring was set to 600 rpm, and the hot plate was set to 40°C under the reaction temperature to avoid overheating of the reactor. The reaction was then left for the desired reaction time, upon which time the reaction was stopped and cooled down by removing the reactor from the heating jacket and placed into a metal stand. The vent tubing was attached to the reactor using a size 16 wrench, and the remaining gases in the reactor were vented. The reactor was opened under a fume hood and the solution was removed with a 10 ml pipette into a falcon tube. The solution was centrifuged for 10 min at 4000 rpm, and two distinct phases were observed representing the hydrocarbon fraction on top of the water produced by the reaction. Using a short Pasteur pipette, the hydrocarbon solution was carefully removed and filtered using a syringe $0.45\mu\text{m}$ PTFE filter into a glass vial in order to remove any catalyst particles. 8 ml of ethanol was added into the remaining aqueous phase, and the solution was filtered with a syringe $0.45\mu\text{m}$ PTFE filter into a glass vial. The weight of each phase was recorded for the yield quantification.

2.4. Analytical Methods

The HDO reactions mixtures were analyzed by Gas Chromatography (GC-FID), with a method that consisted of 1uL sample injection with an injector temperature of 250°C, a 50:1 split, a column ramp of 50°C to 300°C at 15°C/min and a 7 min hold at 300°C, and a He flow into the column of 3.22 ml/min (pressure <14 psi). The gas flows for the FID were: 400ml/min air, 30ml/min of H₂, 25mL/min of N₂ make up. FID temperature was 290°C. The organic sample was prepared by adding 40 mg of the solution into a GC vial containing 1mL of 1mg/ml of dodecane in ethanol standard. The aqueous phase was prepared by mixing 0.5 mL of the solution with 0.5 mL of 2 mg/mL standard dodecane in ethanol solution in a GC vial.

Due to the chemical complexity of the mixture, the effective carbon number (ECN) approach was used with a dodecane standard for the analysis of the samples. The ECN was calculated by the sum of the contributions from each carbon atom multiplied by its contribution factor according to structure, which are shown in Table 1:

Table 1. Contribution factors of various structures to calculate effective carbon number (ECN)(Scanlon & Willis, 1985)

<i>Atom/group</i>	<i>ECN contribution</i>
Carbon-aliphatic	1
Carbon-aromatic	1
Oxygen-primary alcohol	-0.25
Oxygen-secondary alcohol	-0.75
Oxygen-ether	-1

The detailed calculations of response factors of each compound and the corresponding weight are shown below (Scanlon & Willis, 1985):

$$F_{compound} = \frac{MW_{compound} \times ECN_{C12}}{MW_{C12} \times ECN_{compound}} \times F_{C12} \quad \text{Eq. 3}$$

$$M_{compound} = \frac{A_{compound}}{F_{C12}} \quad \text{Eq. 4}$$

where $MW_{compound}$ and MW_{C12} are the molecular weights of the compound of interest and of dodecane, respectively, $ECN_{compound}$ is the effective carbon number of the compound of interest as detailed in Table X, $F_{compound}$ is the response factor of the compound, $A_{compound}$ is the area of the recorded peak of the compound. $M_{compound}$ refers to the mass of the compound of interest.

The yields and the mixture composition were calculated following the equations below:

$$Y_{oil} = \frac{weight_{oil\ phase}}{weight_{LHD}} * 100 \quad \text{Eq. 5}$$

$$Y_{Aqueous} = \frac{weight_{aqueous\ phase}}{weight_{LHD}} * 100 \quad \text{Eq. 6}$$

$$Y_{gas} = \frac{weight_{LHD} - weight_{oil} - weight_{aqueous}}{weight_{LHD}} * 100 \quad \text{Eq. 7}$$

3. Results and Discussion

3.1. Hydrodeoxygenation

Following HDO of LHD at 300°C for 20h with a catalyst loading of 200mg, a clear oil phase and a water phase were formed in the reaction. Figure 11 shows the gas chromatogram of the oil phase following the HDO reactions, with major peaks identified.

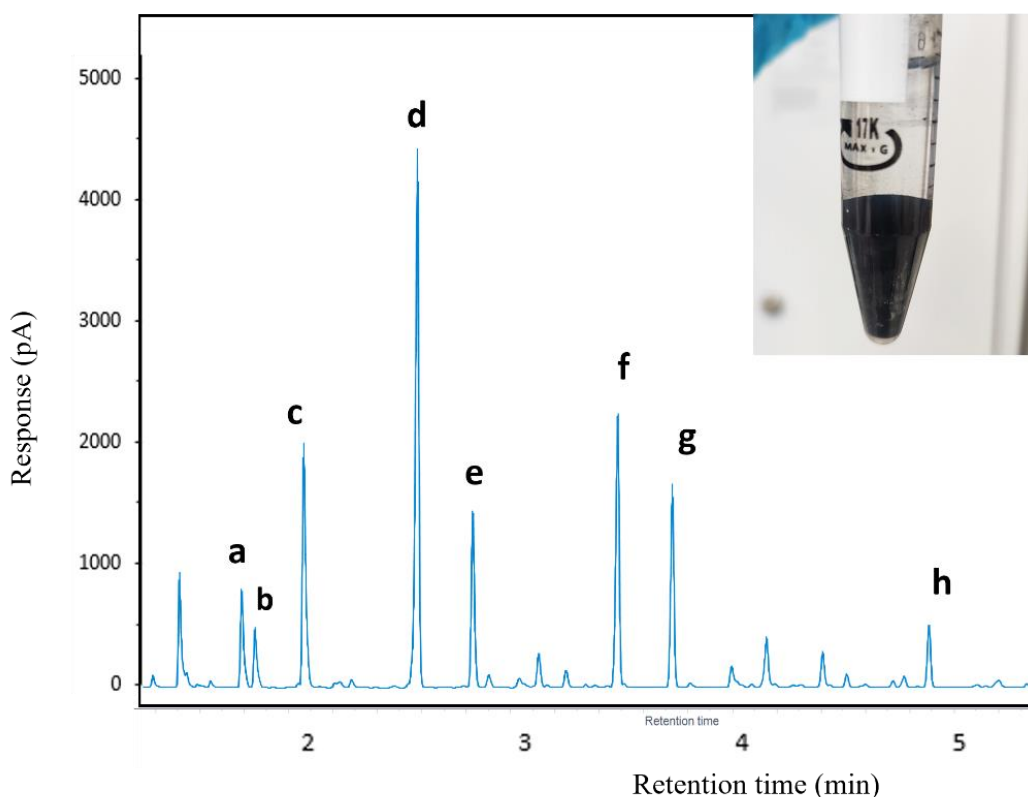


Figure 9. GC-FID spectrum of hydrodeoxygenated LHD SAF oil with major peaks identified and the corresponding species' Effective Carbon Numbers (ECN). Image of two phases formed after HDO reaction, with clear oil phase on top of the water phase containing the Ni/C catalyst

The most prevalent compounds were correlated with major compounds in the LHD feedstock prior to reaction. It was observed that all oxygen-containing groups have been cleaved, while the carbon structure remains unchanged. It was also found that analogous aromatic and saturated species were present, and could result from the same species in the LHD feed.

Under altered reaction conditions, HDO was completed only to a lesser extent, and oxygenated species were observed in the oil following reaction. This change in product was also accompanied by a yellow colour in the SAF oil, which darkened within two weeks in storage under refrigeration. Figure 12 shows the observed results of an incomplete HDO, with the new peaks identified.

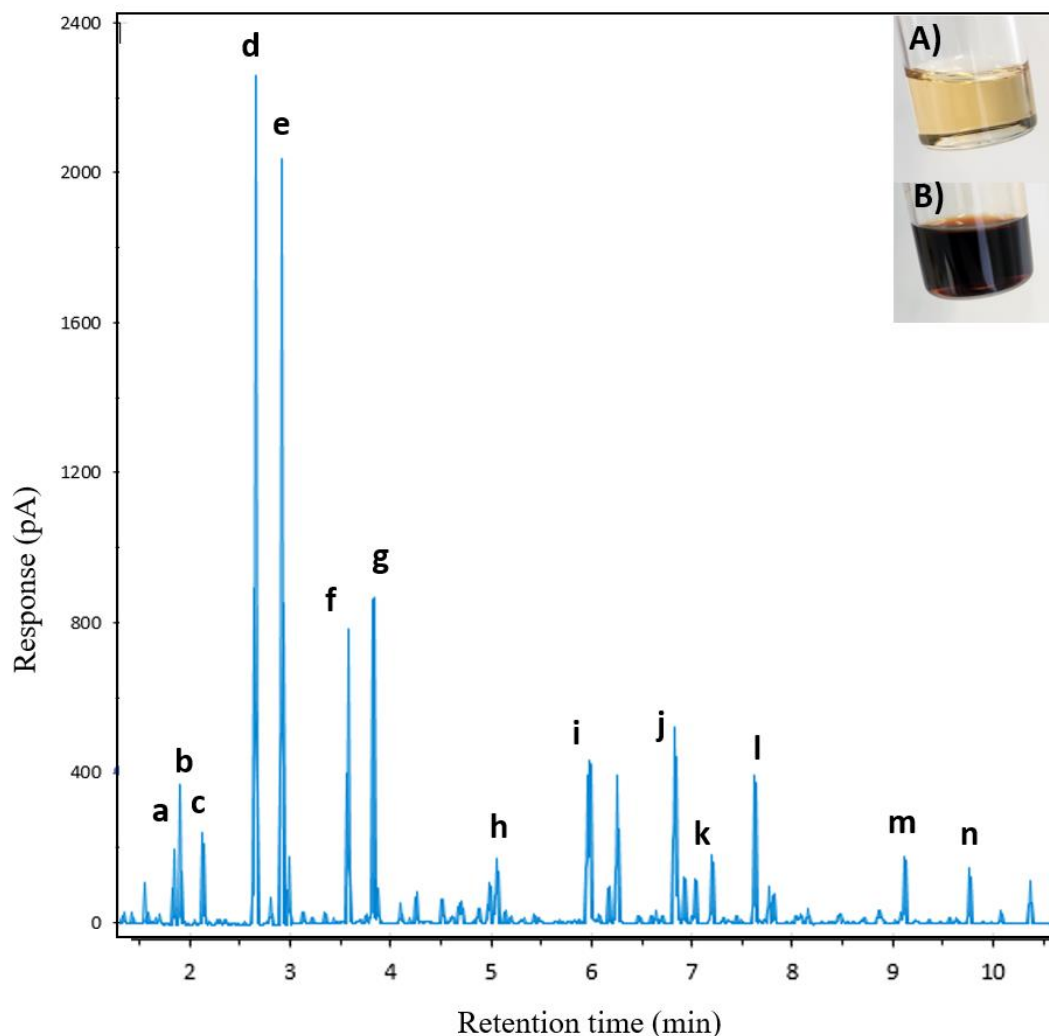


Figure 10. Spectrum showing SAF oil post partial HDO with major compounds identified, as well as a photo of the oil produced A) upon filtration and B) after 2 weeks of refrigeration.

Here, the most prevalent species are the ones previously identified as saturated species and aromatics, however other heavier species are present. These species contain oxygenated and partially deoxygenated monomers. It can be observed that many other

less significant signals appear; approximately 50% of the mass of the oil was identified, although much of this could consist of heavier, non-volatile compounds that are not registered by the GC-FID. These identified species were also linked to major components in the starting LHD material.

From these comparisons, it is possible to observe some of the structural changes undergone by the LHD species during HDO. It can be observed that some carbonyl and hydroxyl groups were removed from the LHD species, while in many cases the methoxylation is preserved unlike in the case of full HDO.

The main types of reactions undergone by the LHD feedstock are HDO reactions, including hydrodemethoxylation and hydrodehydroxylation, and ring hydrogenation reactions. Cracking reactions that produce gaseous products were not observed. In all trials, the desired compounds were the main products of these reactions, suggesting that the rates of competition reactions are small compared to their preceding HDO reactions. A key observation was that the primary hydroxyl groups are more easily activated than those on a phenolic ring, or of methoxyl groups, consistent with previous findings studying the HDO of phenolic systems (Chen et al, 2015; Stone et al, 2022). Many factors could potentially influence the relationship between the relative rates of reaction, which can be explored through the manipulation of HDO reaction conditions.

The resulting mixture contains different types of specie which were identified and divided into major categories. Specifically, one important variable is the proportion of aromatic compounds; many older engines require these compounds, which are less abundantly produced from renewable feedstocks and therefore of high value as a potential SAF additive, while often newer engines do not require these fractions and it is therefore not of interest to produce them (Hileman & Stratton, 2014). Therefore, the ability to tune the production of this fraction would be beneficial to the production of a SAF that is consistent with current infrastructure, and continues to be useful in the case of updated infrastructure. In order to explore potential factors that could influence this distribution, several conditions were investigated.

3.2. Effect of Hydrogen-to-Oxygen Ratio on Product Composition

In order to ascertain the effect of hydrogen present in the HDO reaction, the molar ratio of molecular hydrogen to oxygen fed into the reactor was varied at identical catalyst loading and reaction temperature of 300°C for 20h.

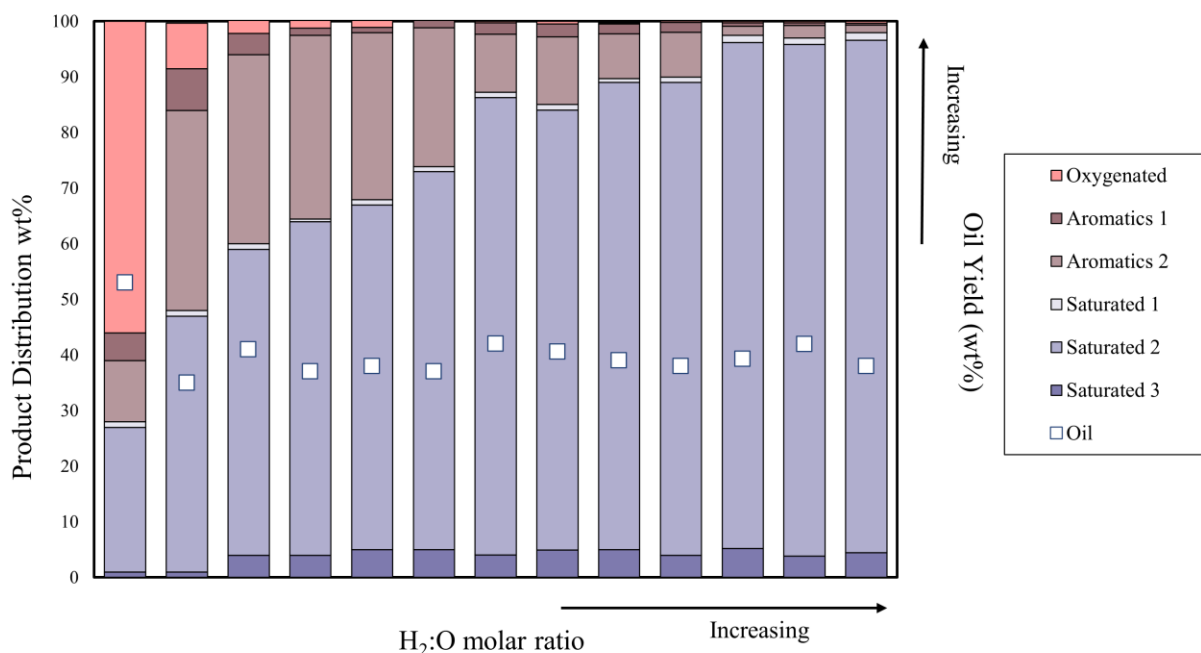


Figure 11. Product distribution of hydrodeoxygenated LHD as a function of the H₂:O ratio in the reaction, performed at 300°C for 20h with 200mg catalyst.

Figure 14a displays the breakdown of the SAF oil composition between the major product categories at each H₂:O molar ratio investigated, as well as the yield of the oil phase present following reaction. This figure displays that with an increase of the hydrogen to oxygen ratio, the product distribution shifts towards the formation of saturated species, and the proportion of oxygenated and aromatic species decreases. This observation is consistent with findings that HDO occurs more readily (i.e. at lower temperatures) when the hydrogen pressure is increased (Maki-Arvela & Murzin, 2017). Certain ratios led to the presence of oxygenated species which are unsuitable for SAF applications. While other ratios led to the production of almost exclusively paraffins, with negligible proportions of aromatics. In this range, the excess hydrogen is participating at greater rates in ring

hydrogenation, rather than primarily being directed into the desired deoxygenation; this condition is therefore not the most efficient deoxygenation condition when this reaction alone is desired. When aromatic compounds are desired, only the small window of hydrogen to oxygen is conducive to the production of these compounds. In conventional jet fuels such as Jet-A, saturated species account for over 70% of the composition, where the aromatic proportion constitutes close to 25% of the total blend; therefore the hydrodeoxygenated samples produced with significant aromatic fractions fall closely in line with the composition of industry standard jet fuels (American Petroleum Institute, 2010). In order to maximize the aromatic fraction while optimizing the use of hydrogen to avoid excess, a certain hydrogen to oxygen ratio is desired. It was also found that the oil yield of the HDO reaction is not significantly affected by changes in molar ratio. Therefore, if paraffins are the main desired product of this reaction, for example in the case of new turbine engines that do not require aromatic compounds, then an optimal hydrogen to oxygen ratio can be used, as this proportion provides an almost-exclusively paraffinic product distribution while limiting the excess of hydrogen and not affecting yield.

3.3. Effect of Temperature on Product Composition and Yield

In order to further optimize the reaction conditions for the tunable production of high-value aromatic compounds, the temperature of the HDO reaction was varied from 275°C to 350°C (Figure 15).

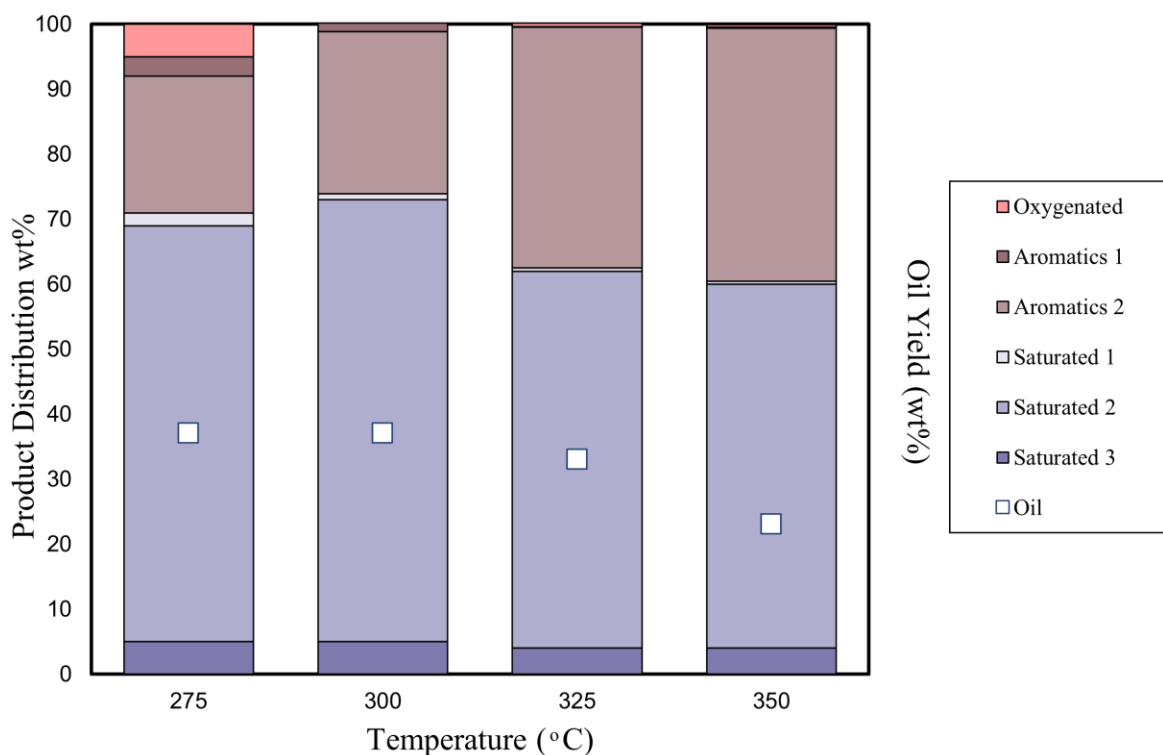


Figure 12. Product distribution and yield as a function of HDO reaction temperature performed at a certain H₂:O ratio with 200mg catalyst after 20h.

It can be observed that temperatures below 300°C were not sufficient to complete the HDO reaction and remove oxygenated species, which suggest that the activation energy of the HDO reactions are higher than other parallel reactions occurring. While the proportion of oxygenated species had significantly decreased from the LHD starting material which contained high amounts of oxygen, HDO could not go to completion at this temperature within this time frame. Species from the starting LHD, were present in very small amounts, but the majority of the oxygenated compounds observed were partially oxygenated. The effect of increased temperature increasing the extent of deoxygenation agrees with previous work using guaiacol as a model compound, where for identical catalyst systems at 300°C it was observed that the main product was phenol, a partially deoxygenated product, whereas at 450°C the main products were fully deoxygenated species such as benzene and toluene (Yang et al, 2016).

The reaction completed at 275°C displayed greater proportions oxygenated species. In addition, the resulting oil from the HDO possessed a green colour that was not present from the reactions at other temperatures, as shown in Figure 16.

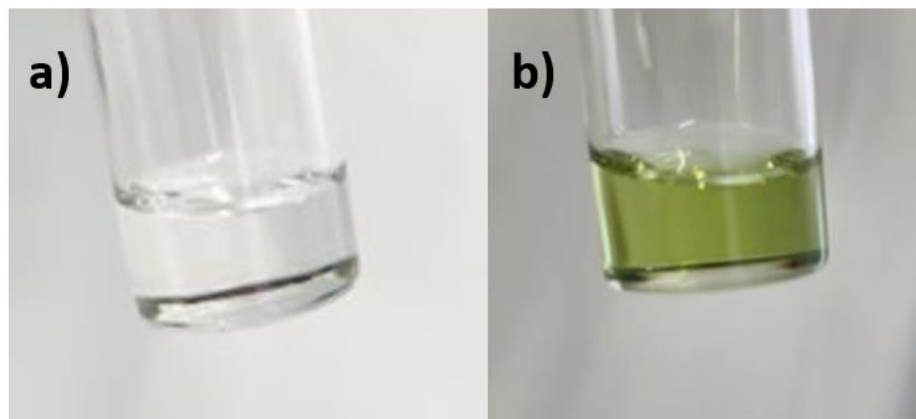


Figure 13. Images of the SAF oil performed at a certain H₂:O molar ratio with 200mg catalyst for 20h at a) 300°C and b) 275°C.

Furthermore, the proportion of compounds identified by GC-FID was far lower for this reaction, meaning that previously unseen compounds including the green one constituted a significant portion of the oil product. It could be hypothesized that the green colour was caused by metal leaching of the catalyst or the reactor material in a potential acidic environment from the feed, which at this lower temperature were not sufficiently deoxygenated and therefore retained their acidic character. This is supported by the lower pH of the SAF products conducted at 275°C of 5 compared to the neutral pH after HDO at 325°C. Further analysis could confirm the nature of these compounds, however in the scope of this work this characterization was not performed as these samples contained oxygenated compounds that render them unsuitable for fuel applications.

Another observation that can be drawn from Figure 15 is that with increasing temperature, the aromatic fraction of the oil increased. This would suggest that the activation energy of the HDO reaction is higher than that of the ring hydrogenation, meaning that at higher temperatures the preservation of aromaticity is favoured. This is supported by conclusions by previous studies of HDO reactions (Heroguel et al, 2019, Yang et al, 2016, Maki-Arvela & Murzin, 2017). In the cases where aromatic fractions are desirable, this could provide valuable information on the tunability of aromatics

production, and allow for optimization. While the aromatics fraction increased with increasing temperature to 350°C, due to material constraints, higher temperatures were not investigated in this study.

However, higher reaction temperatures also resulted in a lower oil yield, and a smaller quantity of liquid phase was observed. A higher gas pressure was also observed following reaction; from this, it can be inferred that the quantity of C-C cleavage was elevated, leading to the formation of more light, gaseous fractions. As such, even when aromatic compounds are desired, the proportional gain due to an increase in temperature may be counteracted by a lower yield when optimizing for their production.

Reactions conducted at 325°C displayed only a small loss decrease in yield as well as an increase in aromatic fraction, therefore this could also be a viable reaction temperature for the production of aromatic compounds. Considering these factors, the 325°C reaction provides 20% more of grams aromatics/kg LHD compared to 300°C. While this is a fairly significant improvement with respect to optimization for the production of aromatics, the increase in temperature may or may not be justified when considering the differential cost and emissions associated with the additional energy to heat the reaction. In order to understand the relative benefits of different operating schemes of the HDO reaction, additional factors influencing the reaction and the energy inputs will be discussed. should be investigated.

3.4. Effect of Reaction Time on Product Composition and Yield

The reaction time was varied in order to analyze the rates of HDO reaction with the eventual objective of optimizing for reduced energy usage.

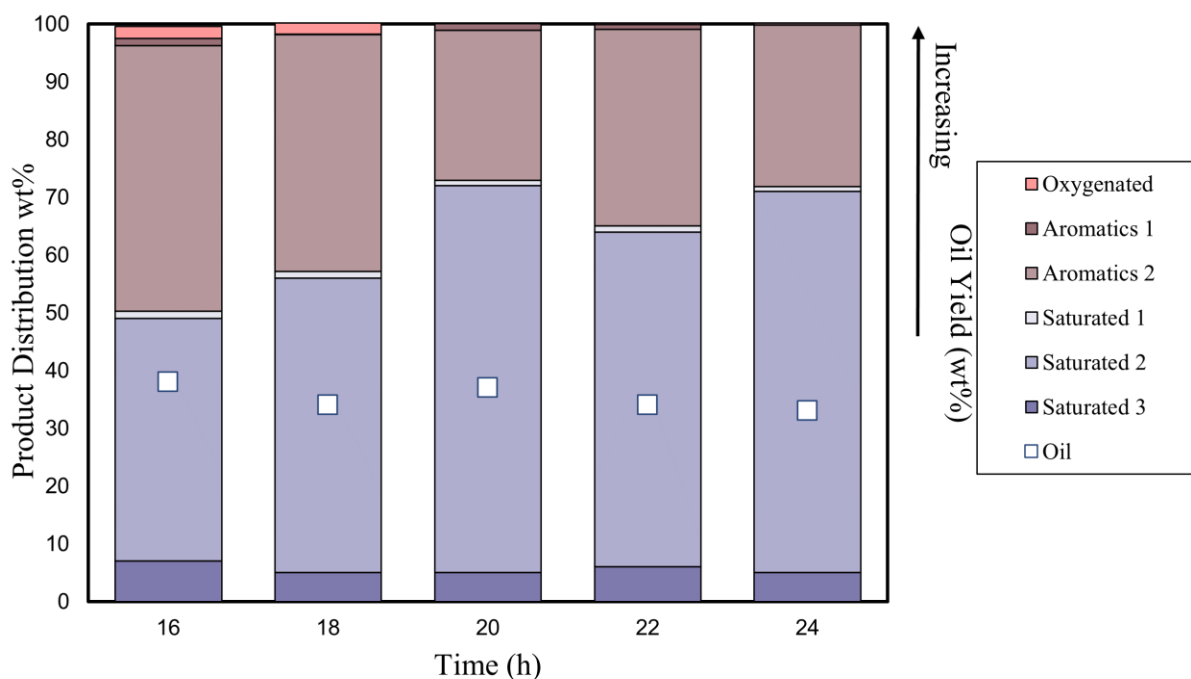


Figure 14. Product distribution as a function of HDO reaction time at a certain H₂:O ratio with 200mg catalyst at 300°C.

A clear trend can be observed that the increase in reaction time leads to an increase in the saturated fraction over the aromatic fraction of the resulting SAF oil. This implies that the ring hydrogenation reaction does not reach an equilibrium, and proceeds following the completion of the HDO; this conclusion is supported the findings using phenol as a model compound (Shin & Keane, 2000). It can also be observed that the HDO is not complete after 18h, suggesting that these HDO reactions are relatively slow, and require around 20h to proceed to complete deoxygenation at this temperature. In addition, there is a virtually negligible decrease in yield over time, suggesting that the rate of cracking is very small.

After 20 hours, it was observed that 275°C was not a sufficient temperature for the complete HDO of the LHD, as oxygenated species were still observed. The question can be posed whether this is due to a slower HDO reaction that would be driven to completion over a greater time frame, or to a system where this reaction would be unfavoured regardless of time. In order to follow up on this question, HDO was performed at 275°C for a 24h period.

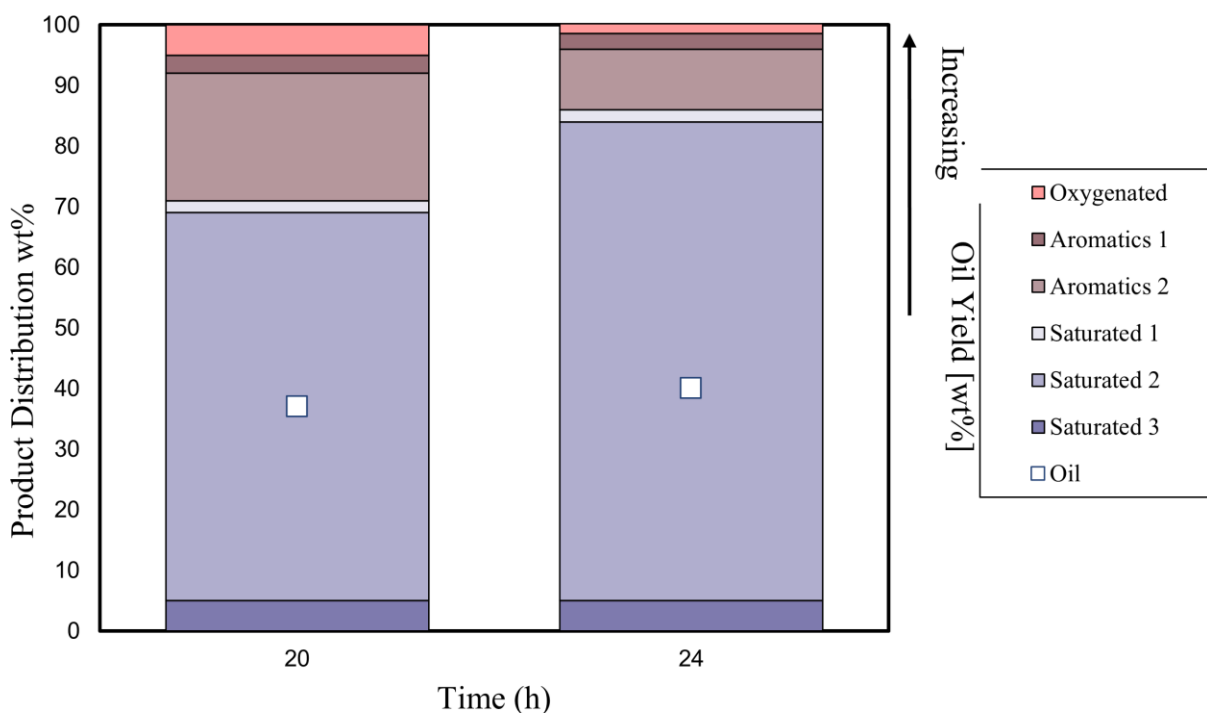


Figure 15. Product distribution as a function of HDO reaction time at a certain H₂:O ratio with 200mg catalyst at 275°C.

As can be observed in Figure 18, a greater proportion of oxygenated species had been converted given the longer time frame, however even with an additional 4 hours of reaction there was a non-negligible proportion of oxygenated species remaining after this reaction. This suggests that without increased temperatures, at this temperature the HDO is kinetically and/or thermodynamically unfavourable compared to ring hydrogenation reactions, and may not ever be complete regardless of reaction time. Longer reaction times to investigate the possibility of complete HDO at this temperature were not attempted, as similarly to the reactions conducted at 300°C, a longer reaction time was shown to be conducive to lower aromatics yield and therefore reaction at 275°C would never be conducive to the production of aromatics. Furthermore, even in a case where aromatics were not desired and the saturated fraction was to be optimized, the energy savings due to the decrease in temperature would quickly be counteracted by the much longer reaction times requiring prolonged heating.

Discarding this possibility for improved energy efficiency through a decrease in temperature, we could investigate the effect of reaction time at a higher temperature and if a shorter reaction time would produce improved results at a lower energy expenditure. It could be hypothesized that, since aromatic fractions were favoured at higher temperatures, and it was seen that at 300°C shorter times favoured this fraction, that these compounds could be even further optimized by a shorter reaction at a higher temperature. The effect of time was explored at 325°C. Due to the relatively low speed of the HDO reactions observed at 300°C requiring a minimum of 20h for completion, HDO trials at 325°C were completed from 18h to 22h (Figure 19).

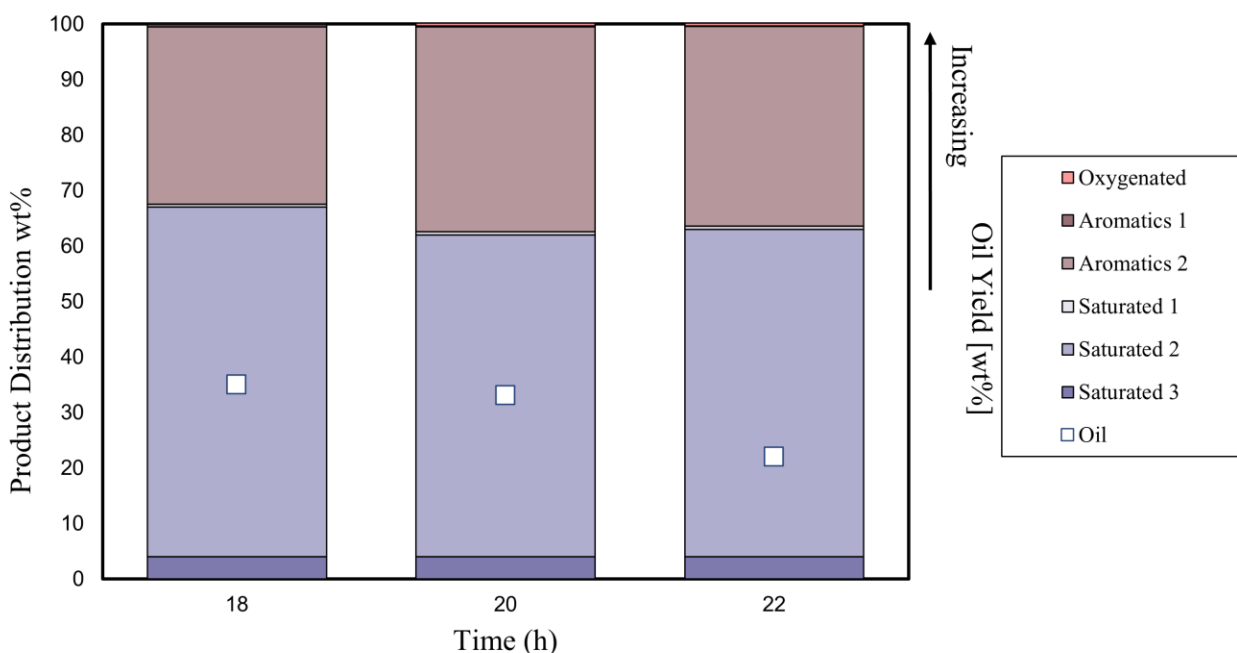


Figure 16. Product distribution as a function of HDO reaction time at a certain H₂:O ratio with 200mg catalyst at 325°C.

It can be observed in Figure 19 that the proportion of aromatics is significantly more stable than was observed at 300°C. This could likely be due to the favourable conditions for the production of aromatic compounds in this temperature regime (Heroguel et al, 2019), as the ring hydrogenation reaction is not favoured at his higher temperature compared to the HDO reactions, and therefore saturation does not continue to occur at a greater extent with longer reaction. It is also evident that there is a decrease in yield with increased time, suggesting that the rate of C-C cleavage is more significant at this

higher temperature, corroborating the findings in Figure 15 and also providing a competitive reaction pathway, potentially contributing to the lower rate of saturation. This also suggests that this reaction is not controlled by an equilibrium with a C-C coupling reaction, and under these more favourable conditions will continue to proceed.

As reactions at both 20h and 18h have comparable aromatics proportions and yields, both could potentially be considered as suitable conditions for aromatics production, in addition to the previously defined condition of 20h at 300°C. As all three conditions fulfill the requirements, the choice of an optimal condition should be made through an analysis of their energy requirements. Although the process design of the current system would be very different in an upscaled form, the energy inputs of the current system can be analysed.

The following assumptions were made for the calculation of energy input: The heating of the reactor was done solely by conduction by a hot plate, which was assumed to be operating at full capacity at all times, and the ceramic fiber jacket of the Parr reactor, which operates at full capacity until the steady state operational temperature is reached. After this point, in the “stationary phase” where the heating jacket operates intermittently to maintain a constant temperature, the fraction of operational time was recorded with a stopwatch and assumed constant.

Table 2. Energy requirements comparison of three different suitable HDO operating conditions for the production of aromatic compounds.

		Case 1	Case 2	Case 3
	T (°C)	300	325	325
	Time (h)	20	20	18
Heat ramp (Jacket)	Power (W)	700	700	700
	Time (s)	2700	3600	3600
	Energy Input (MJ)	1.89	2.52	2.52

Stationary (Jacket)	Time (s)	72000	72000	64800
	Cycle on (s)	1.0	1.5	1.5
	Cycle off (s)	2.50	2.67	2.67
	Ratio on	0.29	0.36	0.36
	Time on (s)	20571	25899	23309
	Power (W)	700	700	700
	Energy Input (MJ)	14.40	18.13	16.32
Hot plate	Power (W)	825	825	825
	Energy in	59.4	59.4	53.5
Total	Energy Input (MJ)	75.69	80.05	72.30
Aromatics (%)	%	27	37	32
MJ/g aromatics	Unit Energy Input (MJ/g)	131.9	132.0	115.7

While the highest proportion of aromatic molecules is generated at 325°C and 20h, the reaction with the lowest energy consumption per unit of aromatics production is 325°C and 18h, with an energy consumption of 115.7MJ/g aromatic molecules. These results are valid with this current system of batch high pressure Parr system; this hot plate is not an optimized heating method as the surface area of the hot plate is only partially in contact with the reactor and therefore unnecessary heat is lost to the environment. Without the influence of the hot plate, the reaction at 300°C and 20h has the lowest heating

requirement and similarly the lowest energy input per gram of aromatics, at 16.3MJ/g. In an upscaled process, a flow reactor would likely be used (Stone et al, 2022), therefore the heating schema would change from what is represented in this system and further optimization would be done for the selection of the optimal process conditions.

In the case that aromatic fractions are not desired, the ideal reaction configuration would be at 300°C for 24 hours; while ring hydrogenation was found to be favoured at lower temperatures, 300°C was found to be the minimum required for HDO. However, the energy requirements for the achievement of this higher cycloparaffin yield would be increased due to the longer reaction time; as discussed in Section 3.2, a better solution would be to increase the hydrogen partial pressure in order to favour ring hydrogenation and all but eliminate the aromatic fraction without the additional heat requirements. If saturated species are the desired product, additional optimization could also be done with respect to temperature at a higher hydrogen pressure; potentially a greater presence of hydrogen could overcome the slower HDO kinetics at a lower temperature.

3.5. Effect of Catalyst Amount on Product Composition and Yield

A last parameter that can be optimized in the operating conditions of the HDO reaction is the quantity of catalyst that is used in the reaction. At the aforementioned optimal conditions for aromatics production of 325°C for 18h at a certain H₂:O molar ratio, the effect of lowering catalyst loading was investigated (Figure 20).

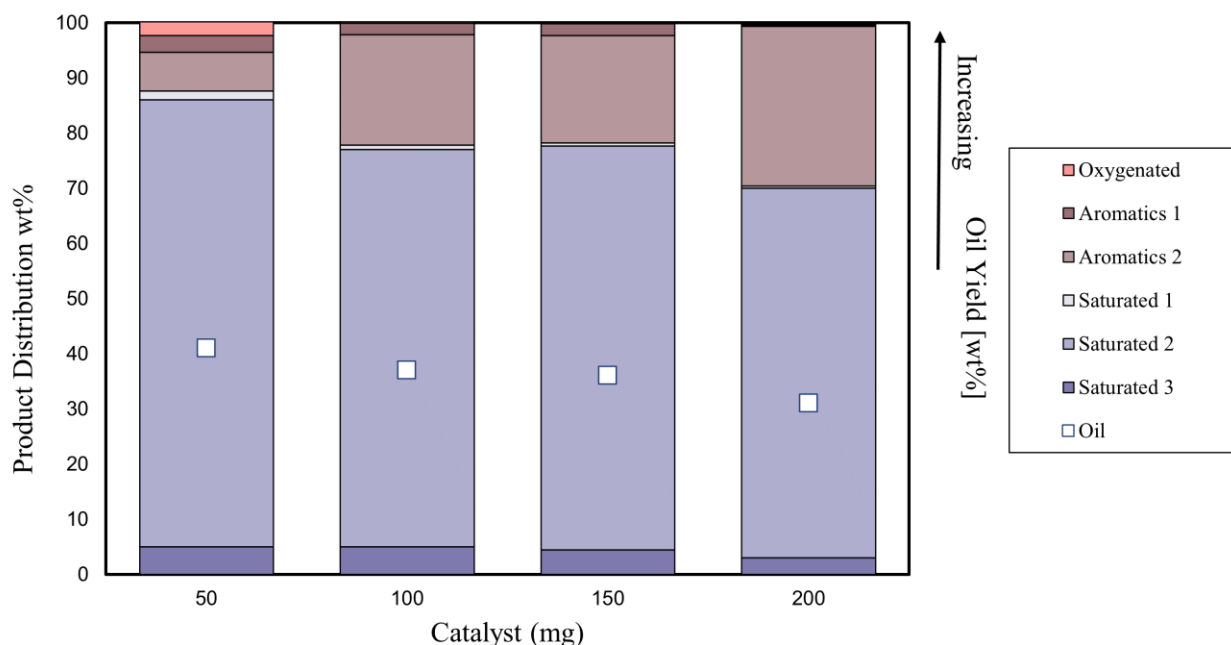


Figure 17. Comparison of HDO using different amounts of Ni/C catalyst at 325°C for 18h at a certain H₂:O molar ratio.

Figure 20 displays the effect of decreasing the catalyst amount from the previously investigated quantity of 200mg. It is observable that complete HDO can be achieved with a catalyst amount of 100mg, however below this not all species are fully deoxygenated. It can be shown that when the catalyst is decreased, fewer aromatic compounds were observed, suggesting that the decrease in catalyst loading and therefore available active sites allowed for favourable conditions for the ring hydrogenation reactions.

Since these reactions are taking place on a heterogenous catalyst, the adsorption and desorption of the reactants on the catalyst surface will influence the rates of reaction. Since these reactions have different stoichiometry in their usage of hydrogen, the dependence of their reaction rates on the available active sites will be different. Without a clearer understanding of the mechanisms and rate determining steps of these reactions, exact quantitative relationships cannot be drawn. However, based on experimental findings, the increase in availability of active catalyst sites favours an increase in the reaction rate of HDO reactions over ring hydrogenation. In comparing

reactions performed with 100mg and 200mg of catalyst, there was an increase of 11% in aromatics production with higher catalyst loading, as well as an increase in cracking reaction by 25%, contributing to a lower oil yield.

Despite a decrease in aromatics production, as all species in the SAF oil were oxygenated even after halving the catalyst, these reaction conditions can still be considered as viable for SAF production. A cost comparison would need to be done for the halving of the catalyst with respect to the slightly smaller amount of aromatics produced, in order to decide a preferential operating mode. If found to be favourable based on the higher oil yield and the price and energy use in generation of the catalyst, 100mg of catalyst could be a possible mode of operation. Conversely, as the proportion of aromatics increases with catalyst loading at only a minimal decrease in oil yield, cost comparisons could dictate whether subsequent increases beyond 200mg could be considered favourable. While the optimal reaction conditions for aromatics production remains 200mg, a decrease in catalyst from 200mg to 100mg would constitute favourable conditions for the optimization of saturation species.

4. Conclusions

4.1. Summary

In this experiment, HDO was successfully implemented to produce SAF-range hydrocarbon from LHD. The SAF oil product composition varied based on reaction operating conditions; a minimum H₂:O molar ratio was identified, temperature of 300°C, and reaction time of 18h were required in order to fully deoxygenate all species such that they could be deemed suitable for SAF applications. These findings gave an indication of the reaction network taking place in order to understand the internal reaction kinetics and tune reaction conditions for the desired products. There are two potential modes of desired operation: where aromatics are favoured, and where saturated species are preferred. The differentiation between these modes is made in relation to whether these fractions are desired in the future for turbine engines; these forecasts are as of yet unclear, however existing demand remains due to the prevalence of legacy aviation fleets.

It was found that an increase of the H₂:O ratio influenced the reactions taking place in two ways: firstly, the proportion of aromatic species decreased with increased hydrogen partial pressure in favour of saturated species, with almost complete removal of the aromatic compounds above an identified ratio. Secondly, below a point, oxygenated species remained in the SAF oil. This implies that the hydrogen partial pressure encourages the HDO until there are no oxygenated species left, after which the excess encourages the saturation of the aromatic ring in accordance with Le Chatelier's principle. Therefore, based on the product needs the reaction parameters could be adapted accordingly.

An increase in the reaction temperature from 300°C to 350°C favours HDO reactions in a higher extent compared to the ring hydrogenation as the preservation of aromaticity in the products is higher. However, the oil yield also decreases with temperature, suggesting that C-C cleavage is also favoured and therefore a greater proportion of products are in the gaseous state. A decreased temperature of 275°C was not sufficient for HDO, regardless of the length of reaction.

It was also observed that an increase in reaction duration at a constant temperature of 300°C led to a decrease in the aromatic fraction, with a very slight decrease in the oil yield. This indicates that at these conditions, the ring hydrogenation is not governed by an equilibrium since aromatic compounds are being transformed into saturated species, and that the rate of C-C cleavage is not predominant. At a higher temperature of 325°C, where the ring hydrogenation reaction is less favoured, a longer reaction time did not lead to a decrease in aromaticity, however the C-C cleavage occurs to a much greater extent over longer reaction times. Based on the current process, the most energy-efficient operation for aromatics production is to conduct HDO at 325°C for 18h, with a unit energy expenditure of 115.7MJ/g aromatics. If this process were to be scaled up and the heating configuration changed, the optimal operating conditions may change and must be re-evaluated.

Finally, it was observed that with a decrease in the catalyst loading, the production of aromatics decreases while the production of saturated species increases along with the overall yield of the reaction. This indicates that the quantity of active

catalyst sites increases the extent to which aromaticity is preserved, as well as catalyzing cracking reactions which preferentially affect the saturated species fraction. Therefore, for the production of aromatic species, a higher catalyst loading should be utilised than that which is optimal for the production of saturated species. The creation of this tunable system through the modification of hydrogen pressure, temperature, reaction time, and catalyst loading, can allow for the production of useful compounds to valorise a coproduct of Bloom's diverse lignin operations while allowing for inherent robustness through adaptation to market trends.

4.2. Assumptions and Limitations

In order to draw conclusions from the data obtained in this investigation, several assumptions were made. In this project, not all experiments were repeated; while some trials were repeated to ascertain reproducibility, due to long reaction times and limited feedstock subsequent experiments were conducted only once. It was assumed that the product distributions obtained in these experiments would be reproducible, however the degree of variation between trials was not investigated and therefore a degree of uncertainty must be assumed. It was assumed that reactions occurred only until the reaction was stopped, after which the product distribution did not change during approximately 1.5h of cooldown time. While this likely overlooks that some reactions could be possible at high temperatures of initial cooldown, this effect would be standardized for all reactions.

To calculate the energy input to the HDO reactions and compare different reaction conditions, it was assumed that all heating was done by conduction, by a hot plate operating at full capacity and a ceramic fiber jacket that operates at full capacity until it reaches the reaction temperature, after which it operates intermittently to maintain temperature in the reactor with a fraction of operational time that remains constant throughout the stationary phase of the reaction. This relies on the assumptions that the room temperature and convection currents of the fume hood remain constant, which can reasonably be assumed in a lab environment.

In addition, several potential sources of error may have affected the results of this investigation. Firstly, throughout the course of these experiments, the means of measuring hydrogen pressure in the reaction was changed due to an instrumentation error. The subsequent method of pressure measurement assumed a constant pressure drop from the pressure gauge on the hydrogen cylinder consistent with previous measurements, which was set to a constant pressure. As reactions continued and the hydrogen cylinder was depleted, a new cylinder with higher pressure was then attached to this same system, throttled to the pressure that had been previously set. The consequence of this is that there were two major shifts in hydrogen pressure recording regimes, which impacted the product distribution of the results following the shift. The trends identified in previous regimes were still consistent with observations under new pressure recording, however new results could not be compared with pre-shift results and therefore relevant experiments were repeated in order to provide relevant comparison.

Another source of error is derived from the limited possibilities for in-house characterization. With a GC-FID as the sole means of analysis, difficulties were experienced in differentiating certain compounds with similar retention times from each other without an additional method of characterization. As a result of this, not all compounds present in the SAF oil mixture had been identified; on average, with the utilized method of analysis, 70-80% of the mass in the oil was identified. This constituted almost all major peaks, however many smaller peaks were present that had not been identified, corresponding to minor products. These less significant compounds were assumed to be insignificant with respect to the overall trends of product distribution, however in subsequent stages of development of this project further analysis would need to be done in order to provide a higher degree of certainty to this process, specifically with respect to the identification of compounds that would not meet relevant standards or carry potential handling risks.

4.3. Safety, Regulatory and Economic Considerations

This work presents initial proof of concept that this Lignin Heavy Distillates stream could be used to create a suitable SAF or SAF additive. However, in order to

formulate and commercialize a product, other considerations must be made with respect to safety, regulatory approval, and economics.

Safety

As SAFs are considered drop-in products to conventional jet fuels, they would therefore possess hazards that are already known; the main hazards associated with conventional jet fuel include flammability, skin irritation, aspiration hazard, and toxicity to aquatic life (Global Companies, 2016). However, there may be additional risks associated with the generated SAF oil which are not yet known, and must be further investigated. Firstly, the generated SAF oil contains 15-30% of compounds that have not yet been identified; in order to ensure that there are no undue dangers associated with this potential product, they must be fully identified and characterized. In the case where there are any toxic or otherwise dangerous substances above which can be accepted, these must be removed, or the process must be reformulated such that they are not generated.

It is forecasted that no to minimal changes are required to existing infrastructure for the implementation of SAFs (Cheng and Brewer 2017). However, in the case that there are any differences between the SAFs and conventional jet fuel in terms of performance, this could also pose safety risks in the use case. Aviation turbine fuels, rather than specifying a particular composition, are mainly governed by their properties and performance, and any deviation with respect to properties such as density, volatility, and freezing point can lead to incompatibilities with current aircraft that could prove dangerous for use (ICAO). While this lignin-derived SAF oil has shown promise in synthesizing the required compounds, further work must be done in performance testing and characterization before it can be considered as a potential SAF and applied for certification.

Additionally, there are hazards present with the synthesis of this SAF, specifically high temperatures and high pressures of hydrogen, a very explosive gas which is very prone to leaking due to its small size. These risks are well managed on a lab scale, through frequently maintained and leak-tested gas connections, an explosion-proof cabinet for storage of the cylinder, and operation within a fume hood to prevent the buildup of explosive gas. However, an upscaled system would need to undergo a thorough review

and frequent oversight for the implementation of safety systems around the storage of a large quantity of hydrogen. Industrial activities involving hydrogen are, however, very commonplace, meaning that successful large-scale strategies exist for the safe handling of hydrogen, and would need to be implemented in this system from safe scale-up and operation (WHA international, 2020).

Regulatory Approval.

Seven SAF pathways exist currently, each with a defined feedstock, processing method, and blend specifications with traditional fuels (European Technology and Innovation Platform, 2022). None of these pathways currently produce aromatic compounds, which contributes to the maximum blend proportion in order to comply with fuel requirements; however, one pathway is currently under review for synthetic aromatic kerosene using sugars (European Technology and Innovation Platform, 2022, Cheng and Brewer, Virent). In order to introduce a new SAF process, an ASTM review process must be completed; this process is extensive, as it involves certification of all elements of a SAF supply chain from feedstock production and collection, to the SAF production plant, to the blend point (ICAO ACT-SAF series,). Some elements of this process can be expedited if these links in the supply chain resemble already-certified processes; another process currently under review involves the upgrading of lignocellulosic biomass by pyrolysis, which if approved could facilitate the approval of an LHD-based SAF (European Technology and Innovation Platform, 2022).

Economics

The largest key question which influences the operation of this HDO process as well as its marketability is the future need for aromatics in jet fuels. While currently most aircraft require aromatic fractions, some new engines do not require this fraction, and if this technology proliferates their demand and therefore the novelty of this lignin-based aromatic-rich SAF would decrease rapidly. It is recognized that, in the short term, these aromatic compounds are desired; even if aromatics-requiring turbines were to be removed from production, for the operating lifespan of the current fleet of aircraft there would be significant aromatic demand, and the minimum potential turnover time of a fleet of aircraft is 14 years (Hileman & Stratton, 2014). The longer-term forecast remains

the topic of speculation; however, a subsidiary of one major oil company with the largest refining system in the USA is developing an aromatics-rich SAF pathway pending ASTM certification, suggesting that major players envisage aromatics as an important part of aviation fuels in the future. This process, under development by Virent, would synthesize aromatic compounds from polysaccharides, rather than utilizing natural aromatic structures as in the case of the proposed LHD-based SAF (Virent, 2023). Currently, a minimum of 8% and a maximum of 25% aromatics are accepted in aviation fuel; given that this process achieves over 30%, the likely solution would be to blend the LHD SAF at approximately a 1:3 ratio with other SAFs that lack this portion; this strategy would lead to a fossil-free fuel, and be capable of fulfilling demand for larger SAF volumes, another challenge facing the SAF sector (European Technology and Innovation Platform, 2022, Cheng and Brewer, 2017)

SAFs are generally accepted as the only CO₂ neutral option to decarbonize the aviation sector, which has committed itself to carbon neutral growth from 2020 on, but it is currently only 0.05% of current aviation fuel consumption (European Technology and Innovation Platform, 2022). There are currently no binding targets for SAF implementation, although the European Commission proposes a 2% minimum by 2025 which increases to 63% by 2050. A main bottleneck to the proliferation of SAF use is the cost as compared to conventional jet fuel: currently, the average price of SAF is 3-9 times that of petroleum-based fuel, where the variance is due to the variety of possible SAF production routes (European Technology and Innovation Platform, 2022). In the case of the proposed LHD-derived SAF, the high pressure and temperature requirements for this fuel would likely lead to a high production cost, even when optimized for scale-up and considering that this fuel is a co-product of other high-value products. Essential to the economic viability of this fuel would likely be its novelty as the only process that can produce the required aromatics, allowing for a higher selling price than other SAF pathways. The disparity between fossil-based fuels and renewable ones is forecasted to persist, so policymakers will be required to implement a combination of quotas, incentives, and carbon prices in order to support the proliferation of SAFs throughout the short-term future (Liebetrau et al, 2019).

4.4. Future work

While this work presents a promising outlook on the potential of this LHD stream to produce a SAF mixture through HDO, further analysis should be done in order to formulate a product and determine its viability.

Firstly, to get a better understanding of the kinetics of the reactions occurring within the HDO system and address the potential source of error with respect to the reactions occurring after the reaction is stopped, it would be of interest to compare the results obtained with an HDO reaction in a flow reactor that allows for continuous sampling during the reaction. This could provide valuable information on the progress of the reaction network and allow for potential further optimization of reaction time.

Secondly, further experiments should be done with respect to catalyst reusability, in order to help avoid excess catalyst waste. Findings of this experiment suggest that increasing catalyst loading beyond the 200mg maximum investigated could favour aromatics production, however, a cost-benefit analysis would be required to determine whether the increased catalyst requirements would be justified. Establishing the degree to which catalyst can be recycled would be an important factor in these decisions. It is noteworthy, however, that in the eventual scale-up of this reaction, HDO would most likely be done with a flow reactor and a fixed catalyst to allow for catalyst reuse; this in turn would require further investigation of the optimal catalyst loading and catalyst lifetime.

Lastly, further characterization should be done of HDO products. Due to in-house equipment limitations, the gas phase present after reaction has not yet been analyzed, and information regarding the composition of this gas through GC-MS could allow us to determine the additional lighter compounds produced by the reaction, and the efficiency of the utilization of hydrogen based on the extent to which hydrogen is still present in the process gas. A comparison of the gas produced by two different reaction conditions with different yields would also give insight into the extent to which c-c cleavage is occurring according to the reaction conditions utilized, and allow the creation of a component balance with respect to carbon, hydrogen, and oxygen which could help to identify the currently unknown compounds. To this end, a greater proportion of the compounds

contained within the SAF oil must be performed; a mass identification of 95% or higher should be achieved before conclusions are drawn with respect to the efficacy of HDO and the suitability of the products for SAF applications. Special attention should be given to identify compounds present to ensure that there are no additional risks for handling and distribution, which could require future separation processes. Finally, in order to formulate a marketable SAF, further characterization must be done of the fuel properties, and additional testing must be done to obtain ASTM certification as a viable SAF.

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