

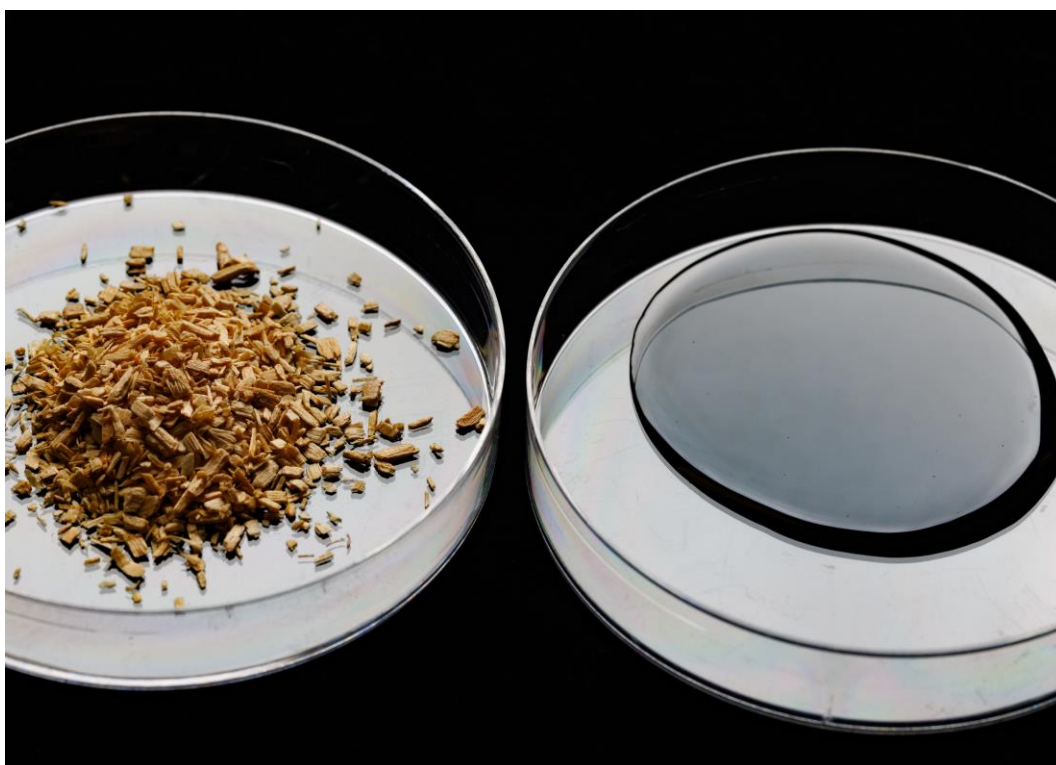


IEA Bioenergy
Technology Collaboration Programme

Direct use of Direct Thermochemical Liquefaction liquids as fuels

IEA Bioenergy: Task 34

June 2025





Direct use of Direct Thermochemical Liquefaction liquids as fuels

Aaron Tay, François-Xavier Collard - Scion, New Zealand

Daniele Castello, Kamaldeep Sharma - Aalborg University, Denmark

IEA Bioenergy: Task 34

June 2025

Copyright © 2025 IEA Bioenergy. All rights Reserved

ISBN, if applicable, here

Published by IEA Bioenergy

Index

Introduction	3
Fuel properties of DTL liquids	4
Pyrolysis-based technologies	4
Definition and scope.....	4
Fast pyrolysis bio-oils	4
Catalytic pyrolysis bio-oils	6
Bio-oils as a drop-in fuel.....	9
HTL-based technologies.....	11
Definition and scope.....	11
HTL biocrude properties and direct utilization as a marine fuel	11
Direct use of HTL biocrude fractions	14
Conclusion and perspectives	17
References	18

Introduction

IEA Bioenergy Task 34 is an International Network of researchers, supporting the advancement and commercialization of bioenergy through biomass direct thermochemical liquefaction (DTL). More than 100 ML of DTL liquids are currently produced per year, with the main use being as substitution for conventional fuel oils in stationary applications [1]. The specifications for Pyrolysis Liquid Biofuel, that are intended for use in industrial burners, are detailed in the Standard ASTM D7544-23. In this standard, the Higher Heating Value (HHV) should be at least 15 MJ/kg and water content is limited to 30% in mass. This standard was developed based on the properties of fast pyrolysis bio-oils, with oxygen contents around 35-40 wt.% (dry).

In the context of DTL research, the production of biofuels, that could replace liquid transportation fuels from fossil origins, has been of particular interest. An essential condition to achieve this goal is to decrease the oxygen content of DTL liquids, so that the HHVs increase to values closer to that of liquid fossil fuels (> 40 MJ/kg). Literature targeting such goal are abundant with hundreds of articles describing novel methods for producing DTL liquids with reduced oxygen content. However, details of the fuel properties of DTL liquids are not commonly reported and compared to values specified in fuel standards.

For an increased use of DTL liquids in the short term, it would be practical to produce drop-in biofuels that could be used with existing carbon-based fuel supply infrastructures. To this aim, the properties of DTL fuels would have to ideally meet current standards required for transportation fuels, with respect to properties such as viscosity, density, pour point, flash point, etc. Alternatively, blending DTL fuels with fossil fuels, to make a hybrid fuel that is within specifications, is also an attractive option to penetrate the market in short term. In this case, miscibility and compatibility of the blended fuels are required.

Recently, much of the focus on DTL liquids has turned towards the hard to abate sectors such as marine and aviation fuels. Some recent technology developments are aiming at producing DTL liquids (with or without upgrading) for marine applications. Regarding aviation fuels, specifications are more stringent and direct production of a compliant DTL fuel appears challenging. Another approach consists in co-refining DTL liquids with fossil oils to produce different types of fuels (e.g. fluid catalytic cracking). To fully evaluate the potential of DTL liquids for fuel applications, the stakeholders need to get detailed information on their fuel properties. Even when DTL liquids are not considered for direct use, but rather as an intermediate for upgrading or co-refining, knowledge of the fuel properties would be important to identify the fuel properties that would need to be improved and the extent of the required upgrading. This report aims at bridging this gap.

The focus of this report is on the fuel properties of DTL liquids. The DTL processes under consideration are single-step fast pyrolysis, hydrothermal liquefaction and solvothermal liquefaction, with or without catalyst. Strategies for further upgrading of the DTL liquids are out of scope and will be discussed in a future report of IEA Bioenergy Task 34.

Fuel properties of DTL liquids

PYROLYSIS-BASED TECHNOLOGIES

Definition and scope

Fast pyrolysis consists of the rapid heating of biomass under inert atmosphere to a temperature typically in the range of 400-600 °C. The yield of the liquid product (bio-oil) is maximised through fast removal of the volatiles released during pyrolysis (short vapour residence time in the pyrolysis reactor) and efficient condensation. Intermediate pyrolysis, which uses relatively lower heating rates, can also be used to target a valuable liquid fuel product, this technology is also considered in this report. Literature research primarily focusses on the conversion of biomass largely composed of lignocellulose, which has a typical composition of 45-50 wt.% C, 40-45 wt.% O and 5-7 wt.% H on dry ash free basis.

The first part of this section is dedicated to pyrolysis without catalyst. The second part will discuss the influence of catalytic treatment. It only considers the liquid product from a single-step process, where the catalytic upgrading of the freshly produced volatiles, in vapour phase, happens either in-situ (inside the pyrolysis reactor) or ex-situ (in a dedicated catalytic reactor). Further upgrading (e.g. hydrogenation) is not considered in this study. The literature study focussed on articles that reported some of the properties of bio-oils according to ASTM and/or ISO standard methods typically used in the fuel industry (e.g. flash point, acid number, etc.).

Fast pyrolysis bio-oils

The study published by Oasmaa and Czernik in 1999 on fuel oil quality provides a basis to describe some fuel properties of pyrolysis bio-oils [2]. According to the study, the water contents of bio-oils are generally determined by Karl-Fischer titration, and range between 15 and 30 wt.%. More recent data confirms that the water contents are mostly (in 83% of the cases) within this range, while it was lower (10-15 wt.%) for 5% of samples and higher (mostly 30-35 wt.%) for 12% of samples. According to ASTM D7544, the maximum water content of bio-oils used in fuel burning equipment should be 30 wt.%.

The high HHV of fossil fuels is due to their largely hydrocarbon composition with only small amounts of other elements such as oxygen. The carbon and oxygen contents are not systematically described in the specifications for liquid fuels from fossil origin. For bio-oil samples, it can give an indication on the energy content and several correlations between the elemental composition and the energy content of bio-oil were developed. Bio-oils with lower oxygen contents generally have higher energy contents. Bio-oils from fast pyrolysis typically have carbon contents of 32-49 wt.%, oxygen contents of 44-60 wt.%, HHVs of 15-20 MJ/kg and Lower Heating Values (LHVs) of 13-18 MJ/kg. Considering that the water present in bio-oil has no contribution to the energy content, it means that the HHV of the organic content (reported as dry basis) is around 20-25 MJ/kg.

An advantage of using lignocellulosic feedstocks as fuel source is their low sulfur content (<0.2%). Consequently, the sulfur content of most of the bio-oils (26 out of 28) were found to be less than 0.05 wt.%. This is considerably lower than the sulfur contents usually found in marine fuels. In light of recent regulatory changes, which limit the maximum sulfur content of VLSFO (Very Low Sulfur Fuel Oil) and ULSFO (Ultra Low Sulfur Fuel Oil) to 0.5 and 0.1 wt.% respectively, blending with bio-oil could help reducing the sulfur content of the residual fuels.

Table 1: Fuel properties of fast pyrolysis bio-oils (without catalyst)

Fuel properties	Unit	Oasmaa and Czernik (1999) [2]	This work (1998-2024)	
			Results	Number of samples
Water content	wt.%	15-30	10-40	94
Density	kg/m ³	1100-1300	1100-1250	66
Kinematic viscosity at 50 °C	mm ² /s	13-80	4-50	54 *
Acid number	mg KOH/g	50-100	65-167	17
Flash Point	°C	50-100	38-103	19
Pour Point	°C	(-36) - (-9)	(-45) - (-9)	23
Carbon residue (CCR or MCR)	wt.%	14-23	16-23	7
Ash content by mass	%	0.004-0.3	< 0.01 - 0.3	49

*Viscosity measured either at 40 or 50 °C, CCR: Conradson Carbon Reside, MCR: Micro Carbon Residue

The acid number of petroleum products can be determined according to ASTM D664. Since the acidity of bio-oils can be caused by different functionalities (i.e. carboxylic acids and phenolics), several authors have suggested method modifications such as changing the solvent and/or titrant (e.g. by using an organic base instead of KOH) for a more sensitive and accurate assessment of the acidity of bio-oils. A titration curve of bio-oil typically shows several endpoints, with the endpoints corresponding to carboxylic acids (often reported as the Carboxylic Acid Number, CAN) coming first, and endpoints from weaker acids (such as phenolics) coming at the end of the titration. It is not always possible from articles to determine whether the reported acid number corresponds to the CAN or the Total Acid Number (TAN). In this review, the acid number of bio-oil was within the range of 65-167 mg KOH/g. This acid number is highly influenced by the content of carboxylic acids such as acetic and formic acids. Acetic acid is sometimes the most concentrated organic compound in bio-oil, with a concentration higher than 10 wt.% (titration of such amount requires around 93.5 mg KOH/g).

From this literature study, the flash points (ASTM D93) of pyrolysis bio-oils vary from 38 to 103 °C, which

is consistent with the range of 50-100 °C, reported by Oasmaa and Czernik [2]. The pour point was found to be between -45 and -9 °C, based on 23 reported results. According to Oasmaa and Czernik, kinematic viscosity (ASTM D445), determined at 50 °C can vary in the range of 13-80 Cst. From 54 results from more recent publications, determined either at 40 or 50 °C, a range of 4-50 Cst was observed, except for one sample, that gave a value higher than 100 Cst. The density at 15 °C was found to be between 1100 and 1250 kg/m³ for 83% of the analyses. Only 8 articles reporting the carbon residue were found. It varied between 16 and 23 wt.%, except for one sample (4 wt.%). The ash contents of most of the bio-oils (72%) were lower than 0.3 wt.%. A few values higher than 1 wt.% were reported from bench scale studies. The use of an optimised vapour cleaning system is expected to reduce the ash content to values lower than 0.3 wt.%, as measured from bio-oils from commercial plants [3].

Sediment in fuel can lead to significant operational failures. For marine fuels, Total Sediment Existent (TSE, ISO 10307-1) is measured by hot filtration under vacuum, and filter washing with non-polar solvents. For pyrolysis bio-oil, a method of vacuum filtration was developed to determine the amount of residue, that is insoluble in a methanol and dichloromethane solution (ASTM D7579). Solid content in fast pyrolysis bio-oil typically varies between 0,01 and 1 wt.%. As the two methods are using different filtration temperatures and solvents, more information is needed to determine if the TSE method is applicable to bio-oils and if there is a correlation between the results obtained from the two filtration methods.

Several aging studies highlighted the reactivity of some chemical groups present in the non-catalytic bio-oils. The reactions observed during long-term storage or accelerated aging (bio-oil submitted to temperatures up to 100 °C) lead to the formation of more water and heavier compounds through polymerization, ultimately resulting in an increased viscosity and, sometimes, the formation of sediments. In the fuel industry, the fuel stability can be assessed according to the Total Sediment Potential (TSP) method. It consists in the hot filtration under vacuum of the fuel, after a 24 h heating at 100 °C (ISO 10307-2), with an allowed maximum value of 0.1 wt.%. TSP results for bio-oil samples are scarcely found in literature.

Different strategies have been considered to reduce the water content and concentrate the organic fraction of the bio-oil (e.g. distillation, solvent extraction). Adding water or inorganic salts to bio-oil can lead to a phase separation. The top aqueous phase has an increased water content and concentrates the more polar compounds (e.g. carboxylic acids, levoglucosan). The bottom phase is more organic (water content can decrease to values lower than 15 wt.%) and has a higher content of lignin-derived compounds. Therefore, the HHV of the organic phase can reach values around 25 MJ/kg [4].

Fractional condensation of the pyrolysis vapours is another approach allowing to isolate several liquid fractions with different properties. Various condensation systems with different numbers of condensers and condenser temperatures have been considered. The first condenser typically contains the heavier compounds, characterised by higher boiling points. Some articles reported the isolation of a fraction with improved properties such as a water content lower than 5 wt.%, an HHV up to 26 MJ/kg and an acid number around 30 mg KOH/g. Such fraction is usually characterised by a particularly high viscosity (up to more than 1000 cSt) [5, 6].

When the volume and/or mass of fuel that is carried is limited, the low energy density of non-catalytic bio-oils or fractions thereof, compared to fossil liquid fuel, is an issue. Solutions are being sought to increase it while simultaneously improving other fuel properties.

Catalytic pyrolysis bio-oils

This section focusses on the catalytic upgrading of the freshly produced pyrolysis volatiles (in-situ or ex-situ configuration), before they reach the condensation system. It does not include the use of hydrogen and further upgrading. Common examples of catalysts used for deoxygenation include zeolites and metal oxides. Following upgrading, the liquid product is typically composed of an aqueous phase (on top) and an organic phase (at the bottom). The aqueous phases generally have water contents higher than 50 wt.% and are separated, due to poor combustion properties. Only articles reporting the fuel properties of the organic phase, separated from the aqueous phase, were considered in this literature study.

The general trend is that an increased degree of deoxygenation will lead to a reduced yield of a product with increased carbon content, stability and energy density [7]. Upgrading under severe conditions (high temperature and catalyst:biomass ratio) can bring the oxygen content to a value lower than 5 wt.%. The impact on fuel properties is discussed in this section.

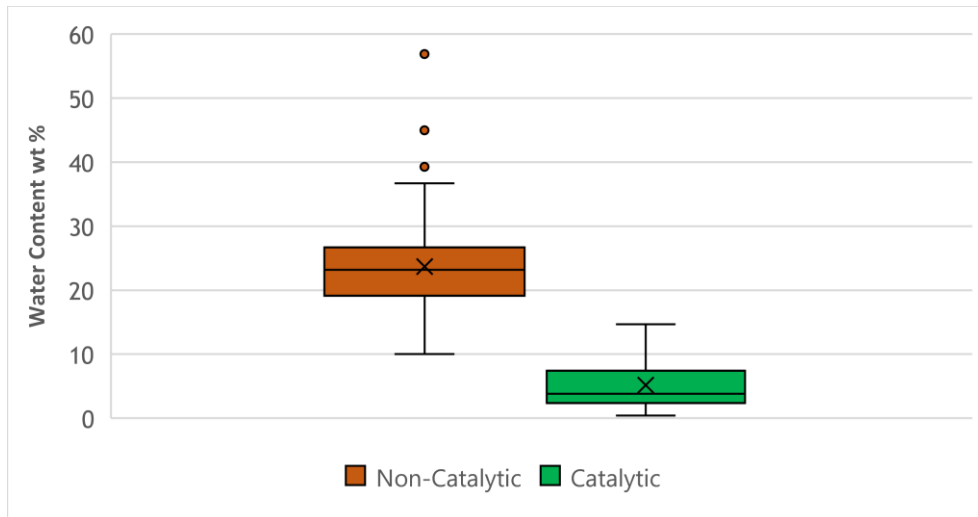


Figure 1: Comparison of the water content in non-catalytic (95 samples) and catalytic bio-oils (94 samples)

Most of the water present in the liquid product is contained in the aqueous phase and the water content of the organic phase is lower than that of non-catalytic bio-oil (Figure 1). It typically varies between 3 and 7 wt.%. Catalytic bio-oils with relatively high oxygen contents and high concentrations of polar oxygenated groups tend to retain more water than more upgraded bio-oils. The energy contents of the bio-oils vary significantly depending on the upgrading severity. Decreasing the oxygen content of the upgraded bio-oil to less than 25 wt.% (or < 20 wt.% on dry basis) can raise the HHV to values higher than 30 MJ/kg.

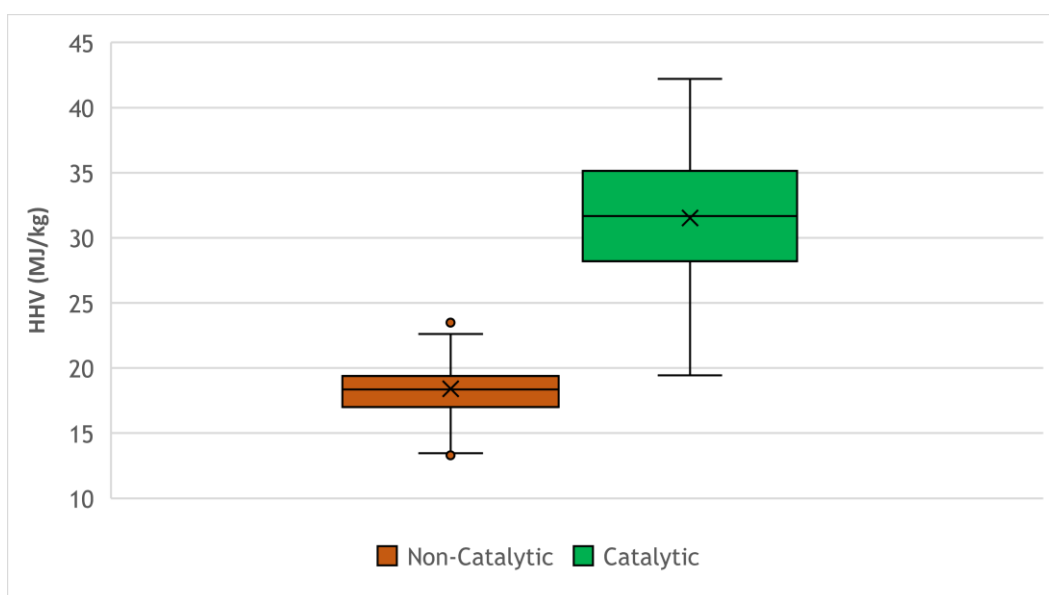


Figure 2: Comparison of the Higher Heating Value (HHV) of non-catalytic (72 samples) and catalytic bio-oils (82 samples)

Catalytic cracking of acidic groups generally leads to a decrease in the Acid number of the upgraded bio-oil (Figure 3). Interestingly, the use of basic catalysts has a more pronounced effect than acidic catalysts. As mentioned previously, the use of different methods to determine the Acid number makes the comparison challenging. However, the pH of the upgraded bio-oils clearly confirms the lower acidity of bio-oils upgraded with basic catalysts.

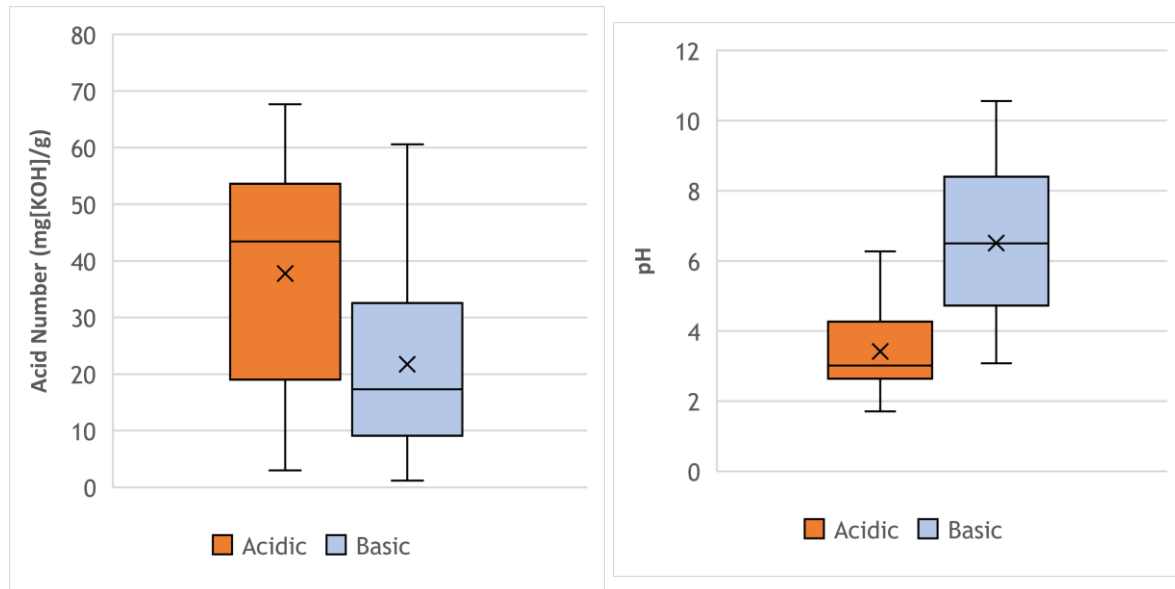


Figure 3: Influence of catalyst type on the Acid number (27 and 25 samples for acidic and basic catalysts, respectively) and the pH of catalytic bio-oil (57 and 31 samples for acidic and basic catalysts, respectively)

The kinematic viscosities of upgraded bio-oils mostly ranged between 28 and 145 cSt, which is higher than the range observed for non-catalytic bio-oils (4-50 cSt). High values are particularly observed for some samples produced through mild upgrading. The decrease in water content, resulting in a fuel with a higher concentration of oligomers, contributes to this evolution. More severe upgrading leads to significant cracking of the oligomers, which tends to decrease the bio-oil viscosity [8]. Despite the reduction in water content, the upgrading of bio-oil tends to lead to a density decrease (932-1157 kg/m³). It can be explained by the catalytic conversion of anhydrosugars with particularly high densities such as levoglucosan (1690 kg/m³).

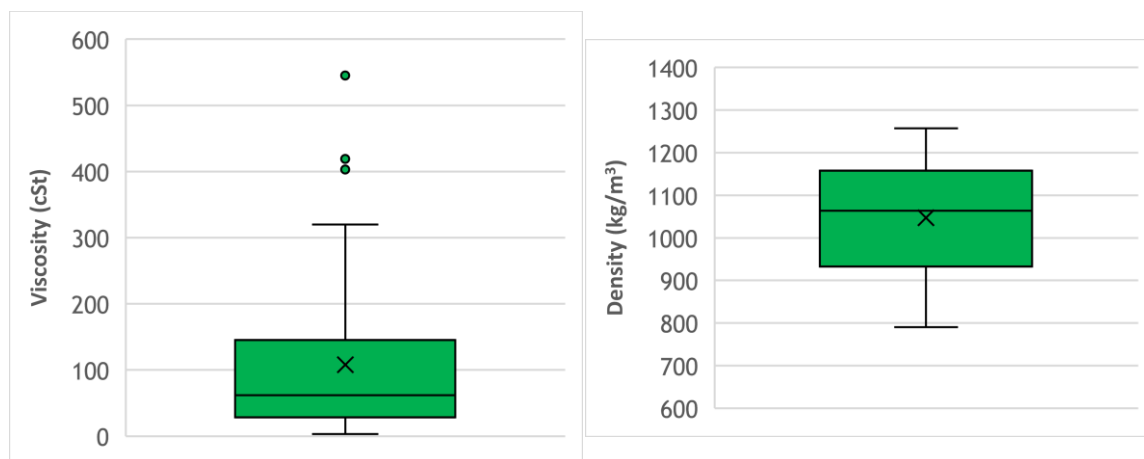


Figure 4: Kinematic viscosity and density of catalytic bio-oils

Limited information has been found on the pour and flash points of upgraded bio-oils. A few results indicate that the pour point tends to be lower than 0 °C. It also appears that the upgrading could lead to a decrease in the flash point temperature, which is consistent with the decrease in the water content. Moreover, extensive upgrading is likely to increase the concentration of light hydrocarbons such as xylene and toluene, which have flash points lower than 30 °C [9].

The ash contents of the upgraded bio-oils were found to be mostly (76% of samples) lower than 0.3 wt.%, with reported values reaching up to 0.6 wt.%. Based on 5 analyses, the carbon residue varies between 10 and 30 wt.%. These results are similar to what was observed for non-catalytic samples.

Several articles reported that bio-oil deoxygenation results in a more stable liquid, as evidenced by aging studies [7, 8]. Increasing the level of deoxygenation leads to limited repolymerization reactions and viscosity change, when the sample is heated. More information would be needed to determine how this trend would translate in terms of stability according to analytical methods used in the fuel industry, such as total sediment existent and total sediment potential.

Bio-oils as a drop-in fuel

Despite the significant improvement of the fuel properties brought by the catalytic upgrading, catalytic pyrolysis bio-oils are hardly used as drop-in fuels in the transportation sector, either because some properties are not within specifications or because the specifications are not adapted to the nature of bio-oil. Catalytic pyrolysis bio-oils are generally composed of molecules with a wide range of molecular weights (up to more than 1000 g/mol). It is clear that some properties (distillation, acid number, density, etc.) are still far from that of gasoline, diesel or kerosene. Marine fuels have less stringent specifications and the substitution of this type of fuel in the short term appears more feasible. Marine fuels are internationally regulated by the norm ISO 8217, which categorizes them into two main classes: distillate and residual marine fuels. Marine distillate fuels are generally clear and bright, with a distillation curve showing that most of the compounds have boiling points lower than 350 °C. Marine residual fuels contain significant amounts of heavy compounds with boiling points higher than 500 °C. As such, DTL liquids, which are composed of products from incomplete depolymerisation (with more than 30 C atoms), could be considered for the substitution of residual fuels. This section compares some properties of catalytic pyrolysis bio-oils and marine residual fuels. The discussion is focussed on the potential use of catalytic bio-oil as drop-in fuels in blends with residual fuels.

Combustion

The latest version of the ISO 8217 (2024) introduced the bio-residual marine fuel, defined as a blend of a petroleum residual marine fuel with bio-based liquid fuel. Typical fuel currently used within this classification are blends of FAME (Fatty Acid Methyl Ester) and VLSFO. For this type of fuel, it is required to report the net heat of combustion, without any specified minimum value. Catalytic pyrolysis bio-oils with net heat of combustions in the range of 30-33 MJ/kg are commonly reported. This is lower than the average value of 37 MJ/kg reported for FAME according to CIMAC (International Council on Combustion Engines). However, considering the density of the respective fuels (860-900 kg/m³ for FAME vs 1050 kg/m³ on average for catalytic bio-oils), some catalytic bio-oils could have a higher volumetric energy density (MJ/L) than that of FAME, which means more energy per volume of transported fuel.

After separation of the aqueous phase, catalytic bio-oils upgraded to reach a net heat of combustion between 30-33 MJ/kg still have an oxygen content higher than 5 wt.% and a water content around 2-5 wt.%. A technique to decrease the water content would be required before blending significant amount with residual fuels, as the maximum for bio-residual fuel is 0.5% by volume.

The ignition characteristics of residual fuels are assessed through the calculated carbon aromaticity index (CCAI). It was developed to detect any anomaly in the relationship between density and viscosity in petroleum fuels. Its applicability to bio-residual marine fuels with different chemical compositions (e.g. oxygen content) has not been established. It is unlikely that this index with its current recommended values could be a reliable method to assess the combustion characteristics of catalytic bio-oils, especially those with densities higher than 1000 kg/m³. An Estimated Cetane Number (ECN) can be calculated based

on the ignition and combustion properties, as determined in a Fuel Combustion Analyser, of a relatively small amount of residual fuel (200 mL). Kass et al. have studied blends of a heavy fuel oil and the organic phase of a non-catalytic bio-oil [10]. They found that, though adding bio-oil decreased the ECN, the values for blends containing 5 to 15% bio-oil were still acceptable for use in two-stroke diesel engines under low-load operating conditions. Similar studies using catalytic bio-oils with much higher energy contents would be useful to assess the benefit of upgrading on the combustion properties.

Density and Viscosity

Depending on the fuel category, the maximum density of a bio-residual marine fuel varies between 955 and 1010 kg/m³. While the densities of some catalytic bio-oils fall within this range, a large proportion had values higher than the limit. Density influences the efficiency of water removal in the fuel cleaning system. The maximum blending ratio of bio-oil could be limited when using bio-oils with high densities.

There are five categories of bio-residual marine fuels with maximum kinematic viscosities of 20, 80, 180, 380 and 500 cSt. The viscosities of most of the catalytic bio-oils (20-150 cSt) fall within this range.

Miscibility and Compatibility

To use blends of bio-oils and residual fuels in the current infrastructure, miscibility of the fuels is required. In their study about blends of non-catalytic bio-oils (organic phase) and residual fuels, Kass et al. analysed the sulfur content of the blends to assess the homogeneity and used the spot test method (ASTM D-4740) to investigate the compatibility [10]. The results appear promising, especially for blends with ≤ 50% bio-oil. More information, especially about the influence of upgrading on miscibility and compatibility (according to TSP), are needed.

A unified method would need to be developed to assess the homogeneity of the blend. It cannot be done through visual observation, as both the catalytic bio-oil and the residual fuel are dark and opaque liquids. While the upgrading is known to improve the bio-oil stability, its impact on the residual fuel stability, which is driven by asphaltene dispersion, is not known.

Abrasive inorganics (i.e. catalyst fines) and corrosive inorganic acids must be limited in marine fuels. According to ISO:8217 (2024), the acid number limit is 2.5 mg KOH/g and inorganic acids are the most problematic. Fuels manufactured from naphthenic crudes with a higher acid number are acceptable for use. Several articles reported the production of bio-oils with acid number lower than 10 mg KOH/g [11-12]. Such bio-oils could be blended at more than 15% with residual fuels with relatively low acid number (< 1 mg KOH/g). As the strongest acids in bio-oil are generally carboxylic acids, with similar strength as naphthenic acids, it is likely that bio-residual fuels made from bio-oil with acid number higher than 2.5 could be acceptable. Some corrosion studies would be needed to confirm.

The parameter to control the catalyst fines in the residual fuel is the content of aluminium plus silicon, which is limited to 60 mg/kg. Vanadium (maximum 450 mg/kg) and sodium (maximum 100 mg/kg) are naturally occurring inorganics in heavy fuels, that are also monitored for corrosion issues. According to ISO:8217, the maximum ash content in bio-residual fuels is 0.15 wt %. These limits appear achievable as several bio-oil and catalytic bio-oil samples were found to have ash content lower than 0.1 wt.%.

HTL-BASED TECHNOLOGIES

Definition and scope

Hydrothermal liquefaction (HTL) is a thermochemical process consisting of reacting biomass with hot compressed water in a liquid or supercritical state. Typical temperatures are between 280 and 400 °C, with pressures between 80 and 300 bar. Water is typically in excess, with usual dry matter content of 15-20 wt.%. Under these conditions, biomass undergoes several reactions such as hydrolysis, decarboxylation, etc., which break down biochemical macromolecules into smaller ones. The process yields a dark viscous product referred to as “biocrude” as a main product, which contains most of the energy content of the original biomass (up to ca. 70%), and a number of side streams: an aqueous phase, solids and process gases.

HTL biocrude has a relatively high concentration of carbon and good higher heating value (HHV). Due to its properties, HTL biocrude is often referred to as a biomass-derived counterpart of fossil crude oil. However, it has also relevant differences, among which are a significant content of heteroatoms (oxygen and nitrogen), high viscosity and significant amounts of inorganics.

In general, HTL biocrude is conceived as a process intermediate. Its properties, though very promising and representing an important step forward in terms of mass densification, are generally not sufficient to suggest its direct utilization as a fuel. Therefore, biocrude is typically subjected to upgrading, generally carried out through catalytic hydroprocessing. According to the severity of the upgrading conditions, some fractions of the product can be used for jet, diesel and marine fuel applications.

This section focuses on the direct uses of HTL biocrude, therefore all those modes of utilization that do not involve the subsequent hydroprocessing step. Two main scenarios will be considered. The first one involves the utilization of HTL as it is. Due to the heavy nature of this product, the only foreseeable application is within the marine field, as a residue fuel. The second scenario deals with the utilization of distilled fractions of non-hydroprocessed HTL biocrude and will explore the possibilities of its utilization as a diesel fuel.

HTL biocrude properties and direct utilization as a marine fuel

One of the possibilities of directly using HTL biocrude is as a marine fuel. This application is especially interesting, because marine fuels generally do not present very stringent specifications as for other transportation fuels. Moreover, typical bunker fuel is a quite heavy and viscous product, which are characteristics that match the properties of HTL biocrude. As explained previously, for the use of the whole HTL biocrude, the focus is on the substitution of the heavy marine residual fuels.

Table 2: Comparison of the properties of HTL biocrudes and marine residual fuels.

	Jensen et al. [13]	Rodriguez et al. [14]	Steinbruch et al. [15]	ISO 8217
Feedstock	Pine/spruce	Forest residues	Waste animal fat	-
Temperature (°C)	400	380-420	330	-
Pressure (bar)	300	300-350	130	-
Residence time (min)	10-15	10-15	60	-
Fuel Properties				
Density @ 15 °C (kg/m ³)	1073	1036	896	< 991- 1010
Viscosity @ 50 °C (cSt)	665 ^a	4460 ^b	21.69	< 500
Acid Number (mg KOH/g)	48.0 ^c	32.27 ^c	1.46 ^c	< 2.5
HHV (MJ/kg)	38.0	38.14	38.8	-
Water (vol. %)	N/A	0.18	6	< 0.5
MCR (wt.%)	N/A	17	N/A	< 18-20
Sulfur (ppm)	195	146	160	1000

^a At 40 °C

^b At 20 °C

^c Total Acid Number (TAN)

It can be observed that, in general, the properties of HTL biocrude are not suitable for their direct utilization as marine fuels, although important differences are present among the biocrudes themselves. In general, biocrudes often show high values of viscosity, sometimes making them particularly difficult to handle. Bioresidual marine fuels are, however, classified into several classes of viscosity, the highest one arriving at 500 cSt at 50 °C.

A critical aspect for the utilization of biocrude as a marine fuel is its acidity, quantified by the Acid Number (AN). The value stated by the norm (2.5 mg KOH/g) is particularly stringent and represents a possible bottle neck for many biocrudes, often characterized by TAN values several times higher. Upgrading processes can reduce TAN in a quite effective way, either by deoxygenating the carboxylic acids or promoting esterification with alcohols. For direct uses, the only possibility is that of blending.

Despite this, biocrudes do have positive aspects compared with fossil bunker fuel, like its relatively low sulfur content. Blends with HTL biocrude could then present lower concentrations of sulfur and fossil carbon, improving the environmental acceptability of the fuel itself.

Blending

The typical properties of HTL biocrudes are normally not sufficient to allow its direct processing as a marine fuel. As discussed above, there are some specifications, like those on acid number and viscosity, that are not easily fulfilled without an actual upgrading step.

Actual applications in the marine field do not generally consider running engines with 100% biofuel, but they are typically considering the adoption of blends between a bio-based feedstock and a fossil bunker fuel. Whereas this approach does not imply the complete substitution of fossil fuels with bio-derived ones, it can still be beneficial to reduce the carbon footprint of the marine sector. From the fuel perspective, this approach offers the advantage of allowing the utilization of off-spec fuels, provided that their blending can ultimately fulfil the specification of ISO 8217.

This approach has been documented in the literature by Rizzo and Chiaramonti [16], who explored the blending of HTL biocrude obtained from municipal sewage sludge with residual marine fuel of the category ISO-F-RMG 380. In their work, they prepared different blends, namely at 10% and 20%, and characterized the resulting mixtures. Only the 10% blend resulted in a homogeneous product, whereas the one at 20% gave a phase separation. The authors therefore suggested a maximum blending limit between 14-16% for this kind of biocrude.

Some properties measured for the 10% blend are reported in Table 3 and compared to ISO 8217 specifications.

Table 3: Comparison of the properties of a marine residual fuel and a 10% blend of the same fuel with HTL biocrude with the specifications stated in ISO 8217. Data are adapted from Rizzo and Chiaramonti (2022) [16].

	Marine residual fuel	10% blend	ISO 8217
Acid Number (mg KOH/g)	0.32	1.43	< 2.5
Ash (wt.%)	0.005	0.137	< 0.1
Sulfur (wt.%)	0.38	0.47	< 0.5
Vanadium (ppm)	6	5.5	< 350
Sodium (ppm)	1	4.5	< 100
Silicon + Aluminum (ppm)	u.d.l.	23	< 60

u.d.l.: under detection limit

It is important to note that, amongst the ISO 8217 properties that were tested in the context of this study, the analyzed 10% blend fulfils the specifications, except for the ash content, which is slightly higher than the stated limit of 1000 ppm. The influence of the HTL biocrude is evident for some properties, among which ash content and AN. For the latter, the addition of 10% sewage sludge biocrude increased the value by almost 5 times, indicating a critical aspect that strongly limits the blending possibilities.

Direct use of HTL biocrude fractions

HTL biocrude especially from lignocellulosic biomass is immiscible with various fossil streams including fossil crude, heavy bunker fuel, marine diesel and straight-run gas oil (SRGO) [17-19]. A possible way to obtain more usable products from HTL without a chemical process of upgrading is represented by fractional distillation. The yield of distilled fractions from HTL biocrudes varies with biomass type and biocrude quality. The fractions cover a range of products from low-boiling compounds (e.g., gasoline) to heavy, non-volatile ones (e.g., residue and asphalt). Despite the dominance of residual fractions, non-upgraded HTL biocrudes typically contain a relatively high proportion of products that can be classified in the diesel-range boiling point (Table 4) [20]. For many feedstocks, such as lignocellulosic and residues, like municipal solid waste, diesel products are dominant among the distillates. In contrast, biocrudes from microalgae biomass contain more low-boiling gasoline fractions.

Table 4: Comparison of yield of distilled fractions from HTL biocrudes from different feedstocks.

Fractions (wt. %)	Gasoline + jet	Diesel	Asphalt + residue
Hoffman [20] (Hard wood)	22.59	30.78	43.13
Sharma [18] (Pinewood)	10.43	22.84	66.14
Liu [21] (Microalgae)	22.91	26.00	51.09
Taghipour [22] (Spirulina platensis)	35.30	15.00	45.40
Kohansal [23] (Municipal solid waste)	7.29	16.00	76.71
Pedersen [24] (Aspen wood)	18.00	25.60	51.80

The gasoline and residue fractions from biocrude contained high amount of oxygenates and aromatics, rendering them incompatible for blending with conventional diesel such as SRGO (Straight Run Gas Oil) [18]. Distilled fractions in the diesel range from HTL biocrude can significantly contribute to meeting the current road transport diesel demand when blended with conventional diesel. Although bio-distillates share similar ultimate and proximate properties with conventional diesel (EN590), their fuel characteristics differ considerably from EN590 fuel specification due to variations in oxygen and nitrogen content, as well as fuel stability (Table 5). These differences limit the ability to blend bio-distillates with standard diesel fuel.

Table 5: Comparison of properties of distilled fractions in the diesel range from HTL biocrudes and conventional diesel.

Properties	Hoffman [20]	Liu [21]	Sharma [18]	Taghipour [22]	Kohansal [23]	Pedersen [24]	Diesel EN590
Feedstock	hardwood	Micro algae	Pine wood	Spirulina platensis	Municipal solid waste	Aspen wood	-
Boiling range °C	250-350	250-325	250-300	275-350	250-350	250-350	-
Density g/cm ³	0.953	-	-	0.936	0.936	-	0.830
Carbon wt%	87.1	77.8	79.5	78.5	78.4	77.8	87
Hydrogen wt%	11.9	8.5	10.3	10.4	10.8	9.2	12.7
Oxygen wt%	1.0	6.8	10.2	5.8	6.3	13.0	-
Nitrogen wt%	-	6.1	-	5.2	4.2	-	0.01
HHV MJ/kg	42.4	35.8	38.8	38.8	40.1	35.2	45.5
AN mg KOH/g	-	-	-	-	-	35.6	-
Viscosity cP	-	-	-	14.2	21.6	-	2.9
C residue wt%	-	-	-	-	0.01	-	< 0.1
Flash point °C	-	-	-	-	138	-	64

Properties	Hoffman [20]	Liu [21]	Sharma [18]	Taghipour [22]	Kohansal [23]	Pedersen [24]	Diesel EN590
Cloud point °C	-	-	-	-	-14.3	-	-2 to -10
Pour point °C	-	-	-	-	- 18	-	-
Cetane index	-	-	-	-	80-96	-	55

Blending

The compatibility of bio-distillates with conventional diesel is essential to ensure the blend performs consistently in diesel engines while meeting regulatory standards for emissions and fuel quality. The distillate fractions obtained from pinewood biocrude were blended with straight-run gasoil (SRGO) in varying proportions to incorporate HTL biocrude into existing refinery infrastructure. It was observed that the heavy fractions (22.84 wt.%), with low oxygenate content and a high aliphatic composition, closely resembled conventional diesel, making them fully miscible with SRGO at any blending ratio [16]. Watson et al. [25] blended bio-crude-derived diesel fractions (selected based on the boiling range) from food waste bio-crude with local gas station diesel at concentrations of 10, 25, and 50 wt.%. They specifically noted that the TAN and N:C ratios were the primary physical properties limiting the potential contribution of the biocrude-based diesel to the finished fuel. In another report, diesel emission profiles were analyzed at various blending ratios containing 10% and 20% HTL distillates in diesel, with diesel engine tests conducted to assess the feasibility of using HTL distillates as blendstocks. However, the straightforward fuel blending resulted in significant deviations from standard fuel specifications, including an increase in sulfur content in the final fuel [26]. It is however important to point out that the contribution in terms of sulfur and nitrogen is a strong function of the biomass feedstock that was utilized to produce the biocrude. In general, these heteroatoms are more common in biocrudes from non-lignocellulosic biomass, such as, for example, manure, algae or sewage sludge.

Kohansal et al. developed a systematic approach for blending bio-distillates with reference diesel to maximize the contribution of HTL-based fuel while ensuring compliance with standard specifications. The results showed that only a minimal proportion of biocrude distillate mixture (approximately 0.3 wt.%) could be blended before reaching the first blend limit, which was sulfur content. This limitation arose due to the significantly high sulfur content in all the biocrude distillates used in this study (ranging from ~1800-2700 ppm), compared to the maximum sulfur content of 10 ppm in EN590 diesel [23].

Conclusion and perspectives

For over 30 years, fast pyrolysis bio-oils have been combusted for heat and power applications. Despite technology developments, the properties of the fuels directly produced by DTL processes are generally not suitable for the full substitution of conventional liquid fuels from fossil origins in current transportation applications. Partial substitution through blending and use in current infrastructure is more and more considered as a short-term way to reduce the greenhouse gas emissions of the transportation sector.

From an energy point of view, the proportion of fast pyrolysis bio-oil that could be blended for transportation application is limited, as its energy density is approximately half of that of fossil fuels. DTL fuels from catalytic pyrolysis and HTL processes have more potential, especially for marine fuel applications. However, the direct use of DTL fuels has not been much explored in the current literature. Research activities should be expanded, in order to identify the critical properties and the achievable blending limits for DTL fuels of different qualities.

Targeting the introduction of significant amount of DTL fuels, careful selection of feedstock and process conditions are required. While most of the DTL fuels from lignocellulosic feedstock present the advantage to have lower sulfur content than that of residual fuels used in the marine industry, some DTL fuels from non-lignocellulosic origin contain significant amount of sulfur and nitrogen. The isolation of specific fractions by solvent fractionation, fractional condensation or distillation has the potential to improve some fuel properties such as narrower distillation range or better miscibility with fossil fuels. Properties requiring particular attention include acid number, water content, miscibility with fuels from fossil origins and compatibility of the resulting blends.

While a fossil fuel with a high acid number can be corrosive, it appears that some of the acidic compounds responsible of the high acid number of DTL fuels are not problematic. There is a need for the validation of a standard test method for the acid number of DTL fuels, which determines the content of the corrosive acids.

The recent updates on the ISO 8217:2024 standard, describing the properties of marine fuels show that the use of biofuels (mostly FAME at this stage) is becoming significant. As the test methods used to characterise the fuel specifications were developed based on fossil fuels, it is likely that some of them are not adapted to fuels from biomass origin and would require some modifications to facilitate the use of DTL fuels.

Among the parameters that are critical for the application of DTL liquids in the marine sector, it is of utmost importance to define clear protocols to evaluate their miscibility with fossil streams. This is especially important for the applications as a marine residual, where the visual evaluation of miscibility is not possible. It is indeed to be expected that DTL liquids will be employed in the form of blends, and the determination of the stability of the mixture is a key parameter in view of commercialization.

References

1. Collard, F.-X., S. Wijeyekoon, and P. Bennett. *Commercial status of direct thermochemical liquefaction technologies*. in *IEA Bioenergy: Task*. 2023.
2. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils State of the Art for the End Users*. Energy & Fuels, 1999. **13**(4): p. 914-921.
3. Bultink, P., et al., *Interlaboratory Study of Sample Homogeneity Impact on CHNS, Water, and ICP Analysis of Biomass Liquefaction Oils*. Energy & Fuels, 2025.
4. Song, Q.-H., et al., *Effective Phase Separation of Biomass Pyrolysis Oils by Adding Aqueous Salt Solutions*. Energy & Fuels, 2009. **23**(6): p. 3307-3312.
5. Pollard, A.S., M.R. Rover, and R.C. Brown, *Characterization of bio-oil recovered as stage fractions with unique chemical and physical properties*. Journal of Analytical and Applied Pyrolysis, 2012. **93**: p. 129-138.
6. Yang, H., et al., *Experimental studies on a combined pyrolysis/staged condensation/hydrotreatment approach to obtain biofuels and biobased chemicals*. Fuel Processing Technology, 2022. **228**: p. 107160.
7. Collard, F.X., et al., *Optimising ex-situ catalytic fast pyrolysis of pine wood at pilot scale: Impacts on the energy content, chemical composition and stability of the liquid fuel product*. Journal of Analytical and Applied Pyrolysis, 2022. **168**: p. 105725.
8. Rowland, S.M., et al., *Thermal Reactivity of Bio-Oil Produced from Catalytic Fast Pyrolysis of Biomass*. Energy & Fuels, 2024. **38**(20): p. 19626-19638.
9. Khan, S.R., et al., *Comparison of synthetic and low-cost natural zeolite for bio-oil focused pyrolysis of raw and pretreated biomass*. Journal of Cleaner Production, 2021. **313**: p. 127760.

10. Kass, M.D., et al., *Stability, Combustion, and Compatibility of High-Viscosity Heavy Fuel Oil Blends with a Fast Pyrolysis Bio-Oil*. Energy & Fuels, 2020. **34**(7): p. 8403-8413.
11. Iisa, Kristiina, et al. *In situ and ex situ catalytic pyrolysis of pine in a bench-scale fluidized bed reactor system*. Energy & fuels, 2016. **30**(3): p. 2144-2157.
12. Zhang, Yuan, et al. *Co-pyrolysis of biomass with Red Mud: An efficient approach to improving bio-oil quality and resourceful utilization of the iron in Red Mud*. Fuel, 2024. **355**: p.129482.
13. Jensen, C.U., et al., *10 - Hydrofaction™ of forestry residues to drop-in renewable transportation fuels*, in *Direct Thermochemical Liquefaction for Energy Applications*, L. Rosendahl, Editor. 2018, Woodhead Publishing. p. 319-345.
14. Rodriguez, J.K. and V.C. Wills, *Forest Residues to Fuels: Unleashing the Potential of Hydrothermal Liquefaction Biocrude*. Energy & Fuels, 2024. **38**(19): p. 18705-18721.
15. Steinbruch, E., et al., *Waste animal fat with hydrothermal liquefaction as a potential route to marine biofuels*. PeerJ, 2023. **11**: p. e16504.
16. Rizzo, A.M. and D. Chiaramonti, *Blending of Hydrothermal Liquefaction Biocrude with Residual Marine Fuel: An Experimental Assessment*. Energies, 2022. **15**(2): p. 450.
17. Pedersen, T.H., K. Sharma, and L.A. Rosendahl, *Understanding and predicting the solubility of biocrude oils*. Fuel, 2020. **271**: p. 117619.
18. Sharma, K., et al., *Detailed investigation of compatibility of hydrothermal liquefaction derived biocrude oil with fossil fuel for corefining to drop-in biofuels through structural and compositional analysis*. ACS Sustainable Chemistry & Engineering, 2020. **8**(22): p. 8111-8123.
19. Sharma, K., et al., *Optimized conversion of waste cooking oil into ecofriendly bio-based polymeric surfactant- A solution for enhanced oil recovery and green fuel compatibility*. Journal of Cleaner Production, 2021. **294**: p. 126214.
20. Hoffmann, J., C.U. Jensen, and L.A. Rosendahl, *Co-processing potential of HTL bio-crude at petroleum refineries – Part 1: Fractional distillation and characterization*. Fuel, 2016. **165**: p. 526-535.
21. Liu, T., et al., *Fractional distillation of biocrude from hydrothermal liquefaction of microalgae: Upgrading of fuel properties*. Algal Research, 2022. **68**: p. 102888.
22. Taghipour, A., et al., *Fractional distillation of algae based hydrothermal liquefaction biocrude for co-processing: changes in the properties, storage stability, and miscibility with diesel*. Energy Conversion and Management, 2021. **236**: p. 114005.
23. Kohansal, K., et al., *Automotive sustainable diesel blendstock production through biocrude obtained from hydrothermal liquefaction of municipal solid waste*. Fuel, 2023. **350**: p. 128770.
24. Pedersen, T.H., et al., *Full characterization of compounds obtained from fractional distillation and upgrading of a HTL biocrude*. Applied Energy, 2017. **202**: p. 408-419.
25. Watson, J., et al., *Towards transportation fuel production from food waste: Potential of biocrude oil distillates for gasoline, diesel, and jet fuel*. Fuel, 2021. **301**: p. 121028.
26. Chen, W.-T., et al., *Renewable diesel blendstocks produced by hydrothermal liquefaction of wet biowaste*. Nature Sustainability, 2018. **1**(11): p. 702-710.

