Lignocellulose Liquefaction to Biocrude: A Tutorial Review

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1. Introduction

After some 40 years of research and development, a few liquefaction technologies are now being demonstrated at 200–3000 tons per year scale to convert lignocellulosic biomass to biocrudes for use as heavy fuel or for upgrading to biofuels. Along the way many concepts have been proposed and discussed in the scientific literature, as reported later in this Review. Some technologies process the biomass in near or super critical water whereas others use a high-boiling organic medium. Some operate purely thermally whereas others apply a homogeneous or heterogeneous catalyst and, occasionally, hydrogenation conditions. The diversity of the technologies and the demonstration of some of them at scale seem to justify a tutorial review of the chemistry, the product quality and emerging technologies involved; hence this contribution.

Liquefaction needs first to be placed in the bigger field of biomass valorization technologies. For quite some years already, a first generation of products is produced at commercial scale from easy and edible feedstock such as starch, sugar, and vegetable oils. The valorization of lignocellulose, for example, as residue from agriculture and forestry, has been slower to come, however. This feedstock is more preferable as it is available in much larger quantities, at a lower price, and with lower environmental footprint.\cite{1–4} Technological developments have been slower because lignocellulose is chemically heterogeneous and recalcitrant and, therefore, requires extensive chemistry and processing for upgrading. Various approaches have been proposed, generally based on two main steps, namely “depolymerization” followed by “deoxygenation”.\cite{1–3,5–10} The depolymerization step proceeds through gasification (> 700 °C), pyrolysis (400–500 °C), hydrolysis (< 200 °C), or hybrid forms of these. It may operate purely thermally or be assisted by chemical or biological catalysts. The subsequent deoxygenation or reforming step(s) generally proceeds through chemical catalysis (100–350 °C) or biotechnology (≈ 35 °C). Liquefaction (or solvolysis) belongs to the depolymerization technologies. It partly cracks and deoxygenates the lignocellulose to a biocrude that can subsequently be upgraded to biofuels by conventional oil refining processes (Figure 1). The liquefaction step is a hybrid between pyrolysis and hydrolysis mentioned above as it relies on the thermal chemistry of the pyrolysis but proceeds in a liquid solvent, as do hydrolysis, and operates at a temperature that is intermediate between both, namely 200–400 °C.

Figure 1. Liquefaction concept (adapted from Ref. \[11\]).

Lignocellulose liquefaction is certainly no new research area. The oil crisis of 1973 spurred much research in the conversion of biomass to biocrude and, eventually, to fuels. Excellent reviews from White et al.,\cite{12} Bouvier et al.,\cite{13} Moffat and Overend,\cite{14} Elliott et al.,\cite{15} and recently Venderbosch et al.\cite{16} provide a nice account of these early developments. Building on Bergstrom and Cederquist’s earlier work,\cite{17} these early processes attempted to digest wood in water in the presence of catalysts and reducing gas. The US Bureau of Mines focused on the use of bicarbonate catalyst and CO\textsubscript{2} \cite{18} whereas the University of Toronto worked on Ni-based catalysts and H\textsubscript{2}.\cite{19} Both processes required temperatures around 340 °C and pressures of 150–200 bar to provide deep digestion of woody biomass. Feeding the biomass to such high-pressure processes represented a sizable technical challenge. This led various institutes to add a pretreatment step at milder temperature and pressure at the front end of the process. The biomass was then fed as...
slurry using single- or twin-screw extruder. The addition of organic solvents such as cresol, creosote oil (a phenolic woody oil), ethylene glycol, and light alcohols and ketones (in supercritical state)[20] improved the yield. The biocrude was also proposed as potential solvent. However, it appeared not to be very stable under liquefaction conditions and to lead to unacceptable heavy and viscous product upon recycling. Tar was also explored as liquefaction medium in combination with noble metals as well as CoMo and NiMo catalysts used in oil refineries.[21]

Liquefaction can also be performed in subcritical water in the absence of reactive gas. The hot water serves simultaneously as dispersing medium, reactant, and acid catalyst. In the 1980s, Shell developed the HydroThermal Upgrading (HTU) process to convert biomass to a biocrude of good quality.[22,23] Biofuel B.V. has demonstrated the process and is offering it now for commercialization. It consists of a first digestion of biomass with water at 200 °C and 30 bar to produce a biomass paste, which is subsequently converted to a biocrude at 330 °C and 200 bar for 8 min. The resulting crude contains 10–15% oxygen and has a heating value of 30–35 GJ t−1. Accordingly, the biomass is deoxygenated by CO2 and H2O elimination, both contributing in comparable extend to the deoxygenation.

The 1990s saw the oil price dropping back to 15–20 $ per barrel of oil (bbl) and saw the interest in bioenergy and biomass liquefaction vanishing. But it did not stand for long as the researched resumed around the turn of the 21st century when the oil price rose again beyond 50 $ per barrel. Fundamental studies are now devoted to unravelling the complex chemistry of the hydrothermal or subcritical water liquefaction, as reviewed for example, by Arai and co-workers[24] and Pedersen and Rosendahl.[25] A variety of organic solvents are also revisited under various conditions, for example, pure or in the presence of acids or bases, hydrogenation catalysts, and reducing atmospheres.[26–28] Some researchers revisited the use of hydrogen-donor solvents that where investigated for direct coal liquefaction. Although these concepts may not be new, recent improvements in experimentation, analytics, and process technologies may eventually deliver the understanding and control that is needed for developing a robust process. High energy prices may then provide an economic environment that is favorable for commercialization.

This Review attempts to extract the main insights and concepts and to discuss them in a tutorial approach. Priority has been given to the illustration of the phenomena rather than to an exhaustive review of all relevant work. This was meant to allow a clearer discussion of trends and insights at the risk of not acknowledging all original work that discovered them. As the field has grown in variety, this Review particularly focuses on a limited corner of the field of liquefaction, namely the thermal liquefaction in high-boiling solvent. We consider here liquefaction that is operated

- at temperatures that are high enough (>300 °C) to depolymerize the biomass, particularly the cellulose, without the need for acid catalysts, and
- using solvents that are heavy enough (with atmospheric boiling points >180 °C) to provide a modest vapor pressure at reaction conditions.

Accordingly, the Review focuses on the production of biocrude and does not discuss the conversion of lignocellulosic sugars to well-defined molecules such as acids, furanics, or polyols. Neither does it discuss the field of hydrothermal liquefaction, which has been abundantly reviewed in the literature already.[24–27] Developments in these areas will only be used as reference or comparison whenever judged useful.

Section 2 will discuss the chemical principle of liquefaction, that is, the role of the solvent, the chemistry of liquefaction, and the role of eventual catalysts. Section 3 will discuss the quality of the biocrude, for example, elemental and chemical composition, molecular weight distribution, physical properties, and potential applications. Section 4 will briefly touch on engineering aspects, for example, feeding systems, product workup, and char withdrawal. Finally, Section 5 will review various process concepts available both at experimental and demonstration scale and will briefly address manufacturing costs.

2. Chemistry

The purpose of liquefaction is to achieve partial depolymerization and partial deoxygenation of lignocellulosic biomass in an inexpensive manner, delivering thereby a cheap biocrude that can be further upgraded to biofuels using conventional refining technologies. As the chemistry of the liquefaction is fairly complex, it seems appropriate to open the section by summarizing some key features of the chemistry and leaving detailed discussions for subsequent sections.

Early thermal analysis studies showed that lignocellulose depolymerizes around 300 °C under inert atmosphere.[28] In contrast, hemicellulose is reported to depolymerize at 250 °C and lignin to crack over a wide temperature range of 300–800 °C.[29]
These behaviors are most representative of pyrolysis and also suggest that lignocellulose should undergo thermal depolymerization around 300 °C in inert solvents. Acidic or basic media may lower this threshold temperatures, for cellulose is known to hydrolyze below 200 °C at low pH values and lignin to depolymerize at similarly mild temperatures at high pH values. The partial deoxygenation generally consists of a combination of dehydration (H₂O elimination), decarboxylation (CO₂ elimination), and decarbonylation (CO elimination). Sugars are particularly prone to dehydration and occasionally decarbonylation. Decarboxylation requires carboxylic acids as intermediates.

Beyond favoring the desired reactions, liquefaction conditions should also prevent undesired reactions, for example, re-condensation and repolymerization of reactive intermediates that would otherwise form solid deposits such as humins and char. The selection of suitable solvent, feed concentration, temperature, and eventual additives such co-catalysts or reducing atmosphere can be instrumental here. All these features will be discussed in more length in subsequent sections.

2.1. Solvent

The first liquefaction parameter to be considered is the reaction solvent. The literature indeed reports the use of many of them but rarely discuss criteria for their selection. Nevertheless, a number of selection criteria can be defined upfront, namely

- effective in delivering high biocrude yield
- easily recoverable from the biocrude product
- low solvent cost
- low impact on reactor cost, for example, by not requiring exotic and expensive metallurgy and not resulting in excessive vapor pressure under operating conditions.

The former two criteria require experimental work to be evaluated. However, the latter two can be addressed up front already.

As for the low make-up cost, one needs to realize that the solvent will be used in roughly tenfold amount of the intake of the biomass to result in a pumpable slurry. Experience indeed shows that solvent added up to a seven to eight times the biomass weight is fully absorbed in the pores of lignocellulose. As solvent cost needs to remain lower than the feed cost, the product of solvent price x solvent consumption needs to remain below roughly 1/10 of the feed price. Consequently, solvents priced similar to the biomass, say at 50–100 $ per ton, need to be recovered and recycled for >90% after each cycle. Solvents that cost >1000 $ per ton (such as alcohols, ketones, esters, etc.),[31] need to be recovered for >99%. The <1% loss includes physical losses as well as chemical degradation. Alcohols and polyols such as methanol, ethylene glycol, or glycerol have been used in a number of studies as, documented in various places in this Review (e.g., Table 1). However, no comment is generally provided on their chemical stability under liquefaction conditions. This simple analysis readily shows the need for operating with very cheap solvents such as water, cheap hydrocarbon streams, or a biocrude fraction, as we will discuss later.

As for the impact on reactor cost, the corrosivity of very acidic or very basic media will require exotic and expensive metallurgy. The same may apply for subcritical water that is renowned for its high dissociation constant and, therefore, high corrosivity, for example, as reported for supercritical water oxidation technologies.[40]

The solvent vapor pressure is also a parameter that can be checked at early stages. When targeting a solvent vapor pressure of <20 bar, liquefaction at circa 200 °C (e.g., acid digestion) can utilize solvents with atmospheric boiling points up to circa 100 °C (Figure 2). However, thermal liquefaction at >300 °C requires solvents with atmospheric boiling points >170 °C. Pressure above 20 bar can be accommodated as well but will require challenging and costly feeding systems, as will be discussed in Section 4.1.

The impact of solvent on the product breakdown is a very critical parameter. The early studies mentioned above evaluated a variety of solvents but rarely in a comprehensive and systematic manner. For instance, Heitz et al.[41] reported a significant solvent effect on the rate of wood liquefaction. Stevens et al.[42] claimed that solvents with “Hansen distance (Rₜ)” to

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**Table 1. Hydrogenation catalysts applied in hydroliquefaction at 300–350 °C.**

| Catalyst      | Solvent     | H₂ pressure at RT [bar] | Ref. |
|---------------|-------------|-------------------------|------|
| PdCo liquid   | tetratin    | 40                      | [32, 33, 34] |
| PdAl₂O₃      | tetratin    | 40                      | [32] |
| PdC          | wood tar    | 100                     | [21] |
| Raney-Ni, Ni-octoate, NiAl₂O₃ | ShellSol | 20                     | [36] |
| Raney-Ni, Ni/SiO₃ | H₂O   | 50                     | [34] |
| Raney-Ni    | 2-PrOH      | 40                      | [32] |
| CoMo         | tetratin    | 100–160                 | [33, 36, 37] |
| CoMo/Al₂O₃   | H₂O         | 50                      | [34] |
| Fe₃O₄ (red mud) | tetratin | 150                    | [38] |
| Fe₂O₃ (red mud) | wood tar | 100                    | [21] |
| FeSO₄         | EtOH        | 50                      | [39] |
| CuCrO₂       | H₂O         | 50                      | [34] |
| CuMgAlO₄     | MeOH        | 160–220                 | [38] |

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**Figure 2. Vapor pressure of solvents under liquefaction conditions.**
coniferyl alcohol" smaller than 15 MPa\(^{1/2}\) lead to low solid yields (<10%) as they allow a good dissolution of the biocrude and the early biomass liquefaction products. However, limited data is provided to corroborate this claim. More recently, a variety of solvents, mainly high-boiling and thermally stable ones, has been evaluated under thermal liquefaction conditions at 310 °C.\(^{[43]}\) The solvents include aliphatic and aromatic hydrocarbons (including refinery streams) as well as phenolic and anisol-type components. Accordingly, high biocrude yield and minimum char yield were achieved with fairly polar solvents, with performance improving from alkanes to aromatics to phenolics. More specifically, the char yield was shown to decrease with decreasing the Hansen distance versus cellulose\(^{[43]}\) and to drop to nearly zero at \(R_h(\text{cellulose}) < 20 \text{ MPa}^{1/2}\) (Figure 3). Water was evaluated for comparison and

![Figure 3. Effect of the solvent parameter on the ultimate char yields (adapted from Ref. [43]).](image)

delivered lower biocrude yields than phenolic solvents. The solvent was hypothesized to affect the selectivity of the liquefaction by solubilizing early, presumably carbohydrate-like reaction intermediates, and preventing thereby their condensation and charing on the surface of unconverted biomass. The solvent effect seemed not to be related to the solubility of the final biocrude because all solvents of the study were shown to solubilize the biocrude at reaction temperature.\(^{[43]}\) Moreover, the biocrude was shown to be stable as it did not undergo condensation and charing reactions at extended reaction times. These yields were observed at full biomass conversion and, therefore, represent ultimate yields. This contrasts with the earlier work of Heitz et al.\(^{[41]}\) that operated at partial conversion and, therefore, representative of the rate of liquefaction rather than its selectivity.

Finally, we need to consider the recovery of the solvent from the biocrude. Solvents that show a large Hansen distance from cellulose, being either very polar (such as water) or very apolar (such as alkanes), appear to spontaneously demix from the biocrude at room temperature. They thereby allow a cheap and easy recovery of the solvent, which has formed the basis of a novel biocrude fractionation approach that will be discussed later in this Review.\(^{[43]}\) Most of the other solvents are partly or fully miscible with biocrude and, therefore, require extensive recovery of the solvent from the biocrude. Recovery may imply distillation for low-boiling solvents. This is fairly easy but costly when considering the large amount of solvent used. Using the concept of distillation resistance presented elsewhere,\(^{[43]}\) the distillation of a tenfold excess of solvent from the biocrude would result in a resistance \(R_{\text{prod}}\) of roughly 50–100 per °C and a corresponding distillation cost of 270–500 $ per ton of biocrude (assuming a \(\Delta T = 10–20\) °C and a production scale of 200 kt a\(^{-1}\)). Distillative recovery of high-boiling solvents would be even more challenging as it may require vacuum distillation and may entrain a sizable fraction of the biocrude as well.

Some solvents may bring additional effects such hydrogen donation to stabilize the biocrude. This aspect will be considered later, when discussing the potential of hydroliquefaction, that is, liquefaction under hydrogenation conditions.

Based on the various considerations discussed above, two classes of solvents can be identified as promising for thermal liquefaction.

- Cheap aromatic refinery streams in the gasoil range for they combine a moderate polarity with a low vapor pressure, a modest cost (<5x the biomass) and fair chemical inertness. Moreover, eventual losses of the solvent into the biocrude would not be real losses as they would eventually end up as fuel component after upgrading of the biocrude to biofuel. In some cases that will be discussed later, the solvent recovery can even be omitted as the liquefaction solvent can also be used as medium for the upgrading of the biocrude to biofuels.
- The gasoil-range fraction of the biocrude, which combines excellent solvency properties with low cost, low vapor pressure and no need for deep solvent recovery as it is part of the product.

Water is not recommended here because its high vapor pressure and corrosiveness would result in high equipment cost. Nevertheless, a hydroliquefaction process is presently being built at commercial scale (see Section 5.4) and may disprove this recommendation in the future.

Similarly, alcohols, polyols, and other conventional oxygenated solvents are not recommended in view of their high cost, questionable chemical stability under liquefaction conditions, and high vapor pressure in case of low-boiling components.

These recommendations will clearly impact the conceptual design of liquefaction processes. This point will be discussed more thoroughly later in this Review (Section 4).
2.2. Thermal chemistry

The chemistry of hydrothermal liquefaction, that is, liquefaction in near/supercritical water, has been the subject of much research over decades. Some key chemical features of the studies are worth summarizing here as they may partly apply to the liquefaction in high-boiling solvents. At the early stage, for example, after 10 s at 320°C or 0.1 s at 400°C, cellulose hydrolyses to oligosugars and smaller oxygenates such as C_{1}-C_{6} sugars, hydroxy/keto-aldehydes, and furanics. At longer residence time (15 min at 400°C), however, secondary dehydration reactions are kicking in, leading to furanics, cyclopent(a)/e)none, and phenolic components. Under these conditions, glucose, lignin, and wood are all converted to a similar phenolic-rich biocrude. At 400°C, the biocrude is reported to be moderately light for carbohydrates and lignin: 80% boils below 540°C and, thereby, is likely to have a molecular weight below 600 Da.

Much less detailed information is presently available for other solvents. A recent study used 2-methylnaphthalene as solvent and applied milder temperatures (310°C instead of 400°C) to minimize the undesired formation of char and gas. Carbohydrate feedstock, that is, cellulose, starch, and glucose, were fully converted in ≈10 min and led to significant amounts of char besides biocrude (Figure 4a). Extended reaction time did not affect the product yields significantly, indicating that the biocrude is fairly stable and does not decompose to more char. The biocrude derived from carbohydrate was moderately heavy with the heaviest components, reaching ≈3 kDa. In contrast, lignin was converted to a heavier biocrude, which reached ≈30 kDa but without significant amounts of char or gas. The biocrude derived from lignin appeared to even contain products that are heavier than the original lignin, which indicates the presence of recondensation reactions in the initial stage of the liquefaction reaction. These findings contrast with those of hydrothermal liquefaction that lead to marginal amount of char from carbohydrates and delivers an equally light biocrude from carbohydrates and lignin.

Similar to the hydrothermal process, the biocrude-made 2-methylnaphthalene shows similar aromatic/phenolic, lignin-like characteristics with carbohydrates and lignin as feed. For instance, $^{13}$C NMR analysis identified approximately 60% of the carbon atoms as phenolic like (105–166 ppm) and ≈25% as paraffinic like (1–54 ppm) irrespective of the feedstock (Figure 4b). However, it should be stressed that the phenolic-like components are meant in the wide sense of the term, that is, they include furanic and phenolic components that cannot be differentiated by means of $^{13}$C-NMR spectroscopy. GC–MS analysis of the lightest fraction revealed the presence of furanic, phenolic, and cyclopent(a)/none species in carbohydrate-based biocrude. However, the furanic species were not observed in lignin-based biocrude. These findings confirm the conversion of carbohydrates to phenolic product beyond the expected furanic products.

2.3. Acid–base catalysis

The liquefaction is not limited to the pure thermal operation described above. The potential of catalysts has also been extensively investigated. Acid catalysts such as H$_{2}$SO$_{4}$ were shown to significantly lower the temperature required for digesting the recalcitrant cellulose. Temperatures as low as 200°C suffice to convert the cellulose to levulinic acid and humins when operating in water. The undesired co-production of humins could be depressed by adding organic co-solvent to the medium. Good performance was reported with the addition of acetic acid or γ-valerolactone. The resulting product consists then of a mixture of monomeric and oligomeric oxygenates. This concept was further exploited by Du mesic and co-workers in a multistep-process concept to convert lignocellulose to levulinic acid, furfural, and lignin, with γ-valerolactone produced by converting furfural or levulinic acid. A similar approach was developed by Wyman and co-workers using tetrahydrofuran as solvent. Sulfolane has also been used to convert cellulose to levoglucosan, levoglucosone, and furfural under acidic conditions. But such approaches will not be elaborated on as they are outside the scope of the production of biocrude.

Biocrudes have also been produced in the presence of acid catalysts and alcohol or polyol solvents operating below 300°C. Solvents include butanol, ethylene glycol, and phenol. However, such solvents are likely to react and be incorporated in the biocrude, an undesired feature that has been only occasionally reported.

Base catalysis is known to favor the depolymerization of lignin. However, it is much less effective in depolymerizing the cellulose. Hence, the use of basic additives is not really lowering the liquefaction temperature. It is rather meant to assist the depolymerization of lignin during thermal liquefaction. For instance, the addition of KOH to wet guaiacol resulted in significant reduction of the vacuum residue, the heavy fraction of the biocrude, without significantly affecting the yield of biocrude, gas, and char: the higher the pH value of the liquefaction medium, the lower the fraction of vacuum residue (Figure 5). However, basic additives appeared to get neutralized by carboxylic acid produced during the liquefaction, which hinders the recycling of the base and results in high base consumption. Basic additives also appeared to catalyze...
the degradation of the biocrude. Recycling of the biocrude with replenishment of the basic additive resulted in excessive formation of char.\[56\]

### 2.4. Hydrogenation and hydrogen transfer

Hydrogenation conditions have also been explored as a means to improve the yield and quality of the biocrude. Much of the earlier studies indeed applied hydrogenation atmosphere, being \( \text{H}_2 \) or \( \text{CO} \), and hydrogenation catalysts to the reactor. Such conditions would presumably stabilize unsaturated reaction intermediates and, thereby, depress consecutive condensation reactions to heavy products and char. New light was shed by recent studies that applied hydrogenation conditions at mild temperature, even though these conditions are more characteristic to the pretreatment or fractionation of lignocellulose than its liquefaction.\[57, 58\] Upon treatment at 180°C in alcohol in the presence of hydrogenation catalyst and, optionally, \( \text{H}_2 \) pressure, the lignin fraction appeared to be selectively removed from lignocellulose and to be converted to a light phenolic oil that consists mainly of monomeric and dimeric components. These conditions favored depolymerization of the lignin, solubilization of the product in alcohol, and finally saturation of the reactive \( \text{C} = \text{C} \) double bonds by \( \text{H}_2 \) or by hydrogen transfer from the alcohol medium. In absence of hydrogenation conditions, the depolymerized product would have undergone repolymerization reactions to form heavy phenolic oil.

It is therefore very tempting to presume that a similar stabilization mechanism applies to the liquefaction reaction at much higher temperatures. It has indeed been shown above that the heaviest components of the biocrude mainly come from lignin and that they undergo partial recondensation to heavier products during the initial stage of the liquefaction reaction. However, this reasoning does not exclude the possibility that the hydrogenation conditions would also work on the carbohydrate fraction of the biomass, for example, by stabilizing reactive carbohydrate derivatives to suppress undesired condensation reactions.

These observations and discussions are consistent with several literature reports on the application of hydrogenation conditions to the liquefaction process. For instance, Vasilakos and Austgen\[32\] explored the impact of hydroliquefaction and hydrogen transfer by processing cellulose in tetralin, a potent hydrogen-transfer solvent used in coal liquefaction, in the absence and presence of hydrogenation catalysts (Pd/Al\(_2\)O\(_3\)) and \( \text{H}_2 \) atmosphere. The addition of Pd to the tetralin/cellulose slurry resulted in higher biocrude yield (from 45 to 53%) and slightly lower oxygen content of the biocrude (from 29 to 27%). This was in absence of \( \text{H}_2 \). Addition of 40 bar \( \text{H}_2 \) further boosted the oil yield to 62% and reduced the oxygen content of the biocrude to 24%. Similar trends were observed with isopropanol as hydrogen-transfer solvent and Raney-Ni as catalyst\[32\] or using a catalyst based on Co–Mo mixed oxides operating in tetralin.\[33\] In another example, Xu and Etcheverry\[39\] converted pinewood in supercritical ethanol in the presence of \( \text{H}_2 \) (50 bar initial) and FeSO\(_4\) as catalyst. At 350°C, the addition of the catalyst increased the degree of liquefaction from 70 to \( \approx 90 \)% and the biocrude yield from \( \approx 40 \) to 62%. The resulting biocrude was rich in phenolic components. Regrettably, however, the authors did not report the molecular-weight distribution of the biocrude. Similar experiments run in the Shell laboratories confirmed the beneficial effect of hydrogenation conditions on oil yields and quality on the liquefaction reaction in both hydrocarbon solvents (e.g., decalin) as well as phenolic solvents (guaiacol).\[59\] The resulting biocrude was lighter and exhibited a narrower molecular-weight distribution in the presence of hydrogenation conditions than in its absence, all other conditions being equal (Figure 6). A list of catalysts investigated for hydroliquefaction is provided in Table 1.

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**Figure 5.** Effect of basic additive on the liquefaction of pine wood in guaiacol (adapted from Ref. [56]).

**Figure 6.** Effect of hydrogenation conditions on the Mw distribution of biocrude and product yields (insert) during liquefaction (birch wood (15 wt %)) in guaiacol in the presence of supported metal catalyst (15 wt %) for 30 min at 70 bar \( \text{H}_2 \) and 310°C\[39\].
Hydrogenation conditions have also been combined with acid-base catalysis. The early studies from the US bureau of mines is a nice example. This lead has been further explored in more recent studies. Yu et al. reported the beneficial effect of combining H2 pressure and NaOH on the liquefaction of bamboo in water. It should be noticed that no classical metal-based hydrogenation catalyst was used here.

Murata et al. converted cellulose and wood flour to hydrocarbons using Pt/Re-doped acidic zealites in water at 400 °C and 65 bar H2. Rapid catalyst deactivation was observed, which is consistent with the poor hydrothermal stability of zealites at elevated temperatures. Lange et al. combined acid catalysis, organic co-solvent and hydrogenation conditions to produce a moderately light biocrude at 200 °C (Figure 7). The biocrude consisted largely of monomeric and oligomeric oxygenates that stretches up to a Mw of ≈ 2 kDa. The hydroliquefaction product contained ≈ 27 wt% oxygen and exhibited an effective H/C eff ratio of ≈ 0.8, which is much more favorable than the ≈ 50 wt% oxygen and H/C eff ≈ 0.4 reported for flash pyrolysis. It also contained > 50 C% of paraffinic-type carbon, as determined by 13C NMR spectroscopy compared to the < 20 C% observed for pyrolysis oil.

Figure 7. Yield and biocrude Mw during the acidic hydroliquefaction of birch wood.46

Needless to stress that, with the possible exception of the cheapest catalysts such as red mud (Fe2O3) and FeSO4, the hydrogenation catalyst will have to be recovered from the biocrude and char for recycling to the reactor until it achieved an overall productivity of > 1000 kg of biocrude per kg of catalyst to limit the catalyst consumption cost to affordable level.46 Catalyst stability could be particularly challenging for hydrothermal operation with catalysts that are based on non-noble metal and/or oxide supports. Such materials are indeed infamous for their degradation in hot liquid water, as reported in the previous paragraph for the hydrothermal liquefaction with zeolite-type catalysts. Operation in hydrocarbon solvents might offer better opportunities as long as the steam pressure generated by the reaction is maintained at sufficiently low levels.

2.5. Kinetics

Kinetic information is still scare for liquefaction processes. It is generally limited to simplified and lumped kinetics. In the case of hydrothermal liquefaction, cellulose digestion has been reported to follow a first-order kinetics. However, the temperature dependence of the conversion rate showed some particularities that have been interpreted as a change in mechanism below or above 360 °C. Indeed, Arrhenius plots show a clear increase in activation energy above 360 °C. The liquefaction of pinewood in guaiacol/water has been shown to also follow a first-order kinetics. The conversion rate increased with temperature with an activation energy of 101 kJ mol⁻¹.

The liquefaction of pine wood in guaiacol/water showed a selectivity towards gas and biocrude products that does not vary significantly with conversion (Figure 8). No evidence was found for the eventual degradation of the biocrude into gas or char. Upon closer inspection, however, the heavier components of the biocrude, the vacuum residue fraction, appeared to be slowly converted into lighter distillate products (Figure 8). Similar observations were made for the liquefaction of model components in methylnaphthalene. Cellulose, starch, and wood showed similar conversion and yield profiles as described above, even though the demonstration is less elegant as in the case of guaiacol/water. Lignin behaved differently, however. Being soluble in methylnaphthalene, unconverted lignin should be considered as biocrude rather than as solid. Upon conversion, it produced barely any gas and char but showed the cracking of the heavy vacuum residue components into lighter distillate components. The modest conversion of vacuum residue into distillates that is illustrated in Figure 8 seems therefore to correspond to the slow cracking of the lignin fraction of the wood. Overall, the liquefaction reaction is proposed to proceed in contact with the solvent, being at the interface between the cell wall and solvent or in the bulk of (part of) the cell wall that is swollen by the solvent. The solvated/swollen part of lignocellulose undergoes fragmentation reactions, either purely thermally or assisted by the solvent for example, through hydrolysis with residual water. When these fragments are effectively removed from the lignocellulose surface, they are converted to biocrude through dehydration reactions and,
eventually, minor fragmentation and/or condensation. Part of the early oligomeric carbohydrate fragments not properly solvated undergo condensation and dehydration reactions to form char on the biomass surface. They, thereby, tend to convert into char. Such a scheme is illustrated in Figure 9.

2.6. Summary

Overall, the liquefaction is believed to proceed via thermal depolymerization or hydrolysis of the carbohydrates and lignin with efficient solvation of reactive intermediates to favor dehydration to aromatics rather than recondensation to char. Solvent selection is critical because of its impact on product yields and process cost, as discussed later. Carbohydrates are responsible for char formation when the liquefaction is carried out using suboptimal solvents. Lignin is responsible for the heaviest liquefied products, the tar. Basic additives assist the repolymerization reaction but may also favor recondensation of heavy products to char. Hydrogenation conditions, including hydrogen transfer, lead to lighter and more saturated biocrude.

3. Product Quality

Much effort has been spent over the years to characterize the biocrude and determine its properties as product or as intermediate for further upgrading. Early work on hydrothermal liquefaction indeed provides information of elemental composition, heating value, acid content, water content, viscosity, or distillation profile. Examples of biocrude characteristics are reported in Ref. [67]. From the late 80ies onwards, however, the researchers have applied a battery of spectroscopic methods to elucidate the chemical nature of the biocrude or related products such as pyrolysis oil and lignin. These include FTIR, hybrid GC–MS and GC–GC, size-exclusion chromatography (SEC), and NMR approaches (13C, 1H, advanced multinuclear, 2D). A nice example of such early analytic studies is the analysis of hydroliquefaction and pyrolysis oils by Meier and co-workers.[68, 69] A recent review devoted to spectroscopic analysis of pyrolysis oil and a detailed analytical study of biocrude are worth mentioning in this context.[70, 71]

In contrast to pyrolysis oil and lignin, the characterization of biocrudes requires prior removal of the liquefaction solvent. This is generally an easy task when the solvent is water or light organic components. Such solvents are readily removed by evaporation and water can also be separated by employing liquid/liquid (L/L) separation. The analysis is more complicated in the case of high-boiling organic solvents, which are generally fully miscible and require elevated temperatures for evaporation. Solvent evaporation could then lead to biocrude degradation and co-evaporation of significant amounts of the biocrude.
A solution for this challenge was found in applying preparative SEC to separate the solvent from the biocrude and allow analysis of the biocrude alone.[71] Preparative SEC further allows to fractionate the biocrude in various Mw fractions, allowing thereby to unravel eventual changes in composition or properties between light and heavy fractions.

3.1. Chemical composition

The elemental analysis is arguably the most common property reported. It is occasionally presented in the form of van Krevelen diagrams that report the H/C atomic ratios versus O/C ratio. In general, biocrude shows an elementary composition around CH$_{0.8-1.2}$O$_{0.3-0.5}$. Although it varies with the process conditions (Figure 10a). It is thereby much leaner in oxygen than wood or cellulose, which are both close to CH$_{1.75}$O$_{0.5}$. The biocrude lost about 50 % of the oxygen and ≈40 % of the hydrogen contained in lignocellulose. In fact, biocrudes have the elementary composition of half-dehydrated lignocellulose. As will be seen below, more characteristics will match those of lignin. Upon fractionation by means of preparative SEC, the heaviest fraction of the biocrude appeared to be leaner in oxygen than the lighter fraction, though both have similar hydrogen content.[71] Biocrude that are produced under hydrogenating atmosphere are generally richer in hydrogen, with compositions up to about CH$_{1.3-1.5}$O$_{0.5}$.[72]

Another very common characterization method is GC–MS that is used to identify the low-Mw products of the biocrude. GC–MS has revealed the presence of various families of components, for example, phenolics, furanics, ketones, carboxylic acid, cyclpent(a)e)none. Complementary to GC–MS is the hydrolysis GC/GC that combines polar and apolar columns to segregate the components in families. This method is applied successfully to pyrolysis[73] and has also been applied to various biocrudes in Shell research centers. However, both GC–MS and GC–GC are used to detect low-Mw distillate-type components (< 300 Da), which often represent a minor fraction of the biocrude.

The chemical functionalities of a full biocrude can be investigated by a few spectroscopic methods. FTIR has been a common method to identify the types of chemical bonds contained. Biocrudes typically show a fingerprint that resembles that of lignin, with evidence for O–H, aliphatic and aromatic >C—H, >C=O of carboxyls or carboxylates, aromatic C=C and, occasionally, >C—O bonds of residual carbohydrates as illustrated in Figure 10d.[71,74]

Although less common, $^{13}$C and $^1$H NMR spectroscopy is valuable for characterizing biocrudes.[69,78] Biocrudes appear to show similar clustering of $^{13}$C NMR peaks, irrespective of the solvent (Figure 10b).[71] Most of the carbon, that is, 60–65 %, consists of unsaturated carbon atoms of aromatic, phenolic, or furanic components. 15–25 % are aliphatic carbon atoms, 10–17 % are saturated >C—O carbon atoms as found in alcohols and carbohydrates, and ≈5 % are unsaturated >C—O carbon atoms of ketones, aldehydes, and acids. Such carbon composition holds equally well for biocrudes based on pure carbohydrates, for example, cellulose or starch, and based on lignin but not for biocrudes derived from lignocellulose (Figure 4).[66] According to $^{13}$C NMR spectroscopy, liquefaction biocrude resembles lignin and is much more aromatic in character than unconverted wood and pyrolysis oils, which are richer in carbohydrates (Figure 10b).

They are also more aromatic than biocrudes produced under reducing atmosphere, which are rich in paraffinic carbon atoms (≈55 C%).[69,79] UV/Vis and fluorescence spectroscopy are also valuable tools to analyze streams that are rich in aromatic components. While underexploited as such for biocrude and pyrolysis oil, a variation has appeared quite valuable. The combination of UV/Vis and refractive index analysis in SEC is particularly interesting as it allows mapping the eventual change in aromativity throughout the Mw range of the product. The signal ratio measured between the two detectors (refractive index (RI)/UV) is indeed a clear measure for the degree of saturation of the product. Kumar et al. showed, for example, that an increase in liquefaction time did not affect the biocrude yield or its Mw distribution, but it resulted in clear decrease in its overall RI/UV ratio, indicating thereby an increase in dehydration and aromatization of the biocrude with time.[80] In contrast, the application of hydrogenation conditions resulted in a biocrude with much higher IR/UV ratio, and thereby higher degree of saturation, than observed in absence of hydrogenation conditions.[46,59] For instance, the RI/UV ratio often reaches values of 1.5–2 under hydrogenation conditions but remains around 0.9 under normal liquefaction conditions after normalization of the RI/UV = 1 for lignin.

3.2. Mw distribution

Early studies have characterized biocrudes like one did for crude oil fractions then, that is, using distillation profiles. More recently, however, SEC has become a common method to determine the Mw distribution of biocrude as it is less labor in-

Figure 10. Characteristic of biocrudes based on elemental analysis (a), $^{13}$C NMR (b), SEC (c), and FTIR (d) (adapted from Refs. [11,71]).
tensive and more effective in characterizing the heaviest fraction of the biocrudes. Accordingly, biocrudes appeared to cover a wide range of Mw that can be related to crude oil fractions.\[47, 71\] For instance, biocrude generally contain a large distillate or gasoil fraction with Mw of 150–300 Da, a significant vacuum gasoil fraction (200–1000 Da), and a significant vacuum residue fraction that stretches over 1 kDa, occasionally up to 20–30 kDa (Figure 10c). SEC appeared invaluable in attempting to tune the process conditions to maximize the gasoil fractions and minimize the less desirable vacuum residue fraction.

3.3. Physical properties

As biocrudes are typically half-dehydrated lignocellulose and, thereby, have a \(\approx 30\%\) higher energy content on mass basis, namely 25–30 kJ g\(^{-1}\) higher heating value (HHV) versus \(\approx 18\) kJ g\(^{-1}\) for wood\[71,74\]. This can be readily estimated from the composition of the biomass using the equation proposed by Gaur and Reed [Eq. (1)], where the concentrations are expressed by mass fraction.\[77\] An even higher heat value can be expected from biocrude made under a reducing atmosphere because of their higher hydrogen content. However, biocrudes are also characterized by a fourfold higher volumetric density than the original lignocellulose, namely 1.1 versus 0.2–0.3 g mL\(^{-1}\). This confers them an overwhelming higher energy content on volume basis.

\[
\text{HHV [kJ g}^{-1}\] = 34.91 [C] + 117.83 [H] + 10.05 [S] – 1.51 [N] \\
\text{– 10.34 [O] – 2.11 [ash] (1)}
\]

As biocrude produced under hydrogenation conditions are richer in hydrogen, they will have a higher heating value. Depending on their heaviness, biocrudes can be a viscous paste or even a solid at ambient temperature. They nevertheless become fluid upon mild heating, for example, above 80 °C, and readily become fluid like a heavy motor oil (< 500 cP).\[67\] The combination of fluidity and high volumetric density makes biocrudes handier to transport and store than solid lignocellulose.

Another important characteristic of heavy streams such as biocrudes is their tendency to coke upon heating. A high coking tendency is undesirable as it leads to fouling in heat exchangers and reactors during further upgrading. The coking tendency is typically expressed as weight fraction of coke residue during a micro carbon residue test (MCRT). Biocrudes often show a coke residue of some 30 wt%, which is high when compared to vacuum gas oil (VGO) that is used as fluid catalytic cracking (FCC) feed (MCRT < 2 wt%) and even the heavier residual fuels used, for example, in marine (MCRT of 10–20 wt%). The coking tendency depends on numerous factors of the biocrude. However, one seems particularly dominant, namely the fraction of heavy components. Good direct correlations have indeed been reported between the MCRT and the fraction of vacuum residue determined by SEC (> 1 kDa), as illustrated in Figure 11.\[49,71\] However, the origin of different correlations reported in different studies is worth further investigations.

3.4. Contaminants

Two types of contaminants are worth discussing, namely acidity and ash. The acidity of hydrocarbon streams is typically expressed by the TAN or total acid number, which is the amount of KOH needed to neutralize the stream. Biocrudes show a high acidity that correspond to a TAN of 50–60 mg KOH g\(^{-1}\).\[67\] Hydrocarbon streams with a TAN above 1 mg KOH g\(^{-1}\) are considered as acidic and corrosive.\[78\] Hence, they cannot be transported or processed in cheap carbon steel but require more expensive metallurgies. The high acidity of the biocrude may be decreased by washing and neutralization treatment.

Other contaminants of potential concern are the ash present in the biomass that may end up in the biocrude. Ash may consist of inert components such as SiO\(_2\), basic components of alkali and alkali earth metals, and, to a lesser extent also transition metals. Woody biomass is generally free of SiO\(_2\) and lean in basic ash. However, grassy biomass is generally rich in both. The fate of ash has been investigated for the thermal liquefaction of pinewood in aromatic solvents. Most of the ash appeared to accumulate in the char, which had an ash content 3–4 wt% compared to 0.2 wt% for the biocrude.\[67\] Upgrading of the biocrude by means of acid cracking, as performed in an FCC, may therefore not suffer from extreme neutralization of the acidic cracking catalyst.

3.5. Potential applications

Considering the various properties detailed above, heavy biocrudes produced by thermal liquefaction resemble the heaviest residual fuel class used, for example, in heavy marine engines or in boilers. It is disadvantaged in terms of viscosity, coking tendency (MCRT) and acidity (TAN) but offers a lower sulfur content that most residual fuels.\[67\] Care should be taken to
ensure that the equipment is compatible with the relatively high acidity of the heavy fuel.

Alternatively, heavy biocrudes resemble atmospheric residues and, thereby, might be compatible for co-processing with heavy fractions of crude oil. For instance, the vacuum distillate fraction could be co-processed in an FCC or hydrocracker unit whereas the heavier vacuum residue fraction could be co-processed in a coker or a residue hydroconversion unit (Figure 12). Here again, care should be taken to ensure that the metallurgy of piping and processing units is compatible with the high acidity of the biocrude.

Such co-processing options have been investigated for pyrolysis oil and lignin, which show quite some resemblance with biocrude and can, thereby, offer valuable insights.

Venderbosch et al. recently reviewed old and recent attempts to upgrade pyrolysis oil by means of FCC, either as pure feed or as blend with VGO. Attempts were made at various scales, from laboratory to pilot scale. The product yields appeared to vary with scale in a way that is not yet properly understood. Nevertheless, a few general insights have emerged. Firstly, the pure pyrolysis oil cracks mainly into coke and light products, that is, gasoline or C₄ gas (LPG). The high coke yield is not surprising when considering the high MCRT of pyrolysis oil. Secondly, co-processing with VGO seems to deliver a better product than expected from the linear combination of yields of pure VGO and pure pyrolysis oil. This led to the suggestion of synergetic effects such as hydrogen transfer from VGO to pyrolysis oil. However, the product yield is still unsatisfactory.

Pyrolysis oil can also be upgraded by means of hydrotreatment. Undesired coking and fouling could then be minimized by applying a two-step operation, that is, a mild hydrocracking followed by more severe hydrotreatment. The mild hydrotreatment appeared to also be valuable for FCC co-processing. Blends of VGO with hydrotreated pyrolysis oil indeed resulted in lower coke yield and higher distillate and gas production during FCC upgrading.

Like pyrolytic oil, lignin can also be upgraded by means of hydrodeoxygenation, as discussed in the literature. In contrast to thermal liquefaction, hydroliquefaction (i.e., under reducing conditions) delivers a lighter and more saturated biocrude. The light gasoline-range saturated oxygenates may be reformed to an aromatic gasoline fraction through conversion over acidic zeolite catalysts as proposed by Dumesic and co-workers whereas the gas-oil-range oxygenates can be subjected to hydrodeoxygenation to diesel components. The heavier fraction can be upgraded to biofuels as mentioned above for thermal liquefaction biocrudes, namely by means of FCC, hydrocracking, and, whenever necessary, by means of residue conversion units. Preliminary evaluation at laboratory scale showed that co-processing hydroliquefaction oil and VGO in a laboratory-scale FCC unit has marginal effect on coke and gasoline yield, much smaller than blending of pyrolysis oil.

Clearly, it is easier to upgrade the distillate fraction of biocrude than the whole biocrude. For instance, Corma and co-workers reported a successful hydrodeoxygenation of the distillate fraction of a biocrude obtained by hydrothermal liquefaction of wood.

Beyond bioenergy and biofuels, biocrudes can also be used for the production of chemicals and materials. For instance, Hu et al. reviewed the potential of liquefying lignocellulose in polyhydric alcohols to produce higher Mw polyols (500–10000 Da) that can be used to prepare various polyurethane (PU) products, such as foams, films, and adhesives. The properties of biomass liquefaction-derived polyols and PUs depend on various factors, such as feedstock characteristics, liquefaction conditions, and PU formulations. Similarly, we are exploring at the University of Twente the potential of biocrudes for thermoplastic applications; a first patent application has been filed.

3.6. Summary

The biocrudes present lignin-like properties in terms of elemental composition, chemical functionality, and Mw distribution. However, their high Mw, high viscosity, high acidity, and high coking tendency may hinder application as residual fuel or as precursor for biofuel manufacture. More work is needed to achieve cost-effective valorization.

4. Engineering Aspects

So far, we have mainly discussed the chemistry of thermal liquefaction processes. However, a number of engineering aspects warrant discussion.

4.1. Feeding systems

Feeding lignocellulose to a liquefaction reactor presents very important challenges, as experienced and reported for the early pilot plants mentioned earlier. These challenges have been nicely summarized by Dai et al.

Part of the challenges can be attributed to the properties of the biomass. For instance, the low density of the biomass (typically 0.1–0.2 t m⁻³) typically requires the need to displace a
very large volume of gas or liquid when feeding the biomass “visually dry” or as slurry. The particle size/shape, degree of moisture, and compressibility are also of importance as they affect friction and flowability of the biomass.\[92\]

However, other challenges are due to the need for the biomass to overcome three barriers during feeding, namely pressure, temperature, and medium (gas/liquid). The pulping and paper industry has tackled the challenges and developed methods to feed solid biomass into a liquid-full reactor operating at \( \approx 20 \) bar and \( \approx 200 \) °C. This is generally performed by slurrying the biomass in water and, subsequently, pumping the slurry into the hot pressurized reactor. Similar solutions are indeed considered for biomass pretreatment processes. However, liquefaction processes often imply higher feeding barriers, for example, higher temperature, higher pressure, and/or hazardous environment (flammable or explosive gas or liquid).

Numerous feeding devices have been considered, following a series of decisions to be made.\[92\] One choice is about “dry” versus slurry feeding. “Dry” feeding avoids the need to cool and heat large volumes of solvent but may present challenges to control pressure and gas loss when feeding against high pressure. Another choice involves the feeding capacity versus pressure head.\[92\] For instance, conveyor belt and rotary valves can move very large volumes but cannot overcome high pressure heads: up to \( 10,000 \) m\(^3\)/h\(^-1\) at atmospheric pressure for the belt or up to \( 500 \) m\(^3\)/h\(^-1\) and 15 bar for the rotary valves. In contrast, piston feeders can reach 150 bar but are limited to 100 m\(^3\)/h\(^-1\) capacity. Screw feeders, on the other hand, seem to be limited for both by operating up to 15 bar and up to 50 m\(^3\)/h\(^-1\). To bring these numbers in perspective, a large-scale liquefaction plant with biomass intake of 500 kta\(^-1\) requires a feeding rate of 60 t/h\(^-1\) or 300–600 m\(^3\)/h\(^-1\).

### 4.2. Product workup

Liquefaction processes require separation of the liquefaction solvent from the biocrude, to allow recycling the solvent to the liquefaction reactor. Solvent distillation may be the first option coming to mind if it would not require the evaporation of \( 80–90 \) wt% of the stream to be recovered. Such evaporation duty clearly results in high energy consumption and large distillation columns. As mentioned earlier (Section 2.1), the distillation of a tenfold excess of solvent from the biocrude would result in a distillation resistance (\( \Omega_{\text{prod}} \)) of \( \approx 50–100 \) per °C (see Ref. [45] for more details) and a corresponding distillation cost of $270–500 per ton of biocrude (assuming a \( \Delta T = 10–20 \) °C and a production scale of 200 kta\(^-1\)). Distillative recovery of high-boiling solvents would be even more challenging as it may require vacuum distillation and may entail a sizable fraction of the biocrude as well. Nevertheless, solvent evaporation has been demonstrated experimentally for a biocrude produced by thermal liquefaction in guaiacol.\[64\] This was achieved by atmospheric distillation of water and light organics, followed by vacuum distillation of guaiacol. The vacuum stage was meant to avoid excessive temperature to avoid degradation and condensation/coking of the biocrude at the bottom of the distillation column.

However, alternative fractionation approaches can also be considered. In the case of hydrothermal liquefaction, the aqueous medium can be recovered by spontaneous L/L split of the solvent from the biocrude. Such split and recycling of the aqueous stream may, however, build up organic components to a level that makes the biocrude miscible in the aqueous phase and, thereby, hinder the spontaneous L/L split.

In another alternative, nanofiltration has been demonstrated to recover light aqueous/organic fractions from a biocrude for an acidic hydroliquefaction scheme.\[49\] Nanofiltration was successful in permeating the water, light organic and strong homogeneous acid while retaining the components with Mw above \( \approx 250 \) Da. Such scheme appeared very promising for recycling the solvent mixture and the acid back to the liquefaction reactor, as will be discussed later.

Alternatively, phenolic solvents can be recovered using L/L extraction with temperature-swing (T-swing) solvent recovery.\[81\] Upon contacting with a highly apolar paraffinic stream or a highly polar water-rich mixture at \( \approx 80 \) °C, a heavy biocrude spontaneously splits into a heavy insoluble raffinate fraction and an extractate stream that contains the light soluble biocrude fraction. Upon cooling to ambient temperature, the extractate spontaneously split into light biocrude and clean paraffin or water-rich solvent. The effectiveness of such fractionation method has been rationalized using standard polymer solubilization theory.\[44\] It has been proven effective for recovering and recycling the light biocrude to the liquefaction reactor, approaching steady state in solvent and biocrude quality after a couple of recycle.\[76\] The concept was also applied for the liquefaction of pine wood in light cycle oil, where the biocrude was recovered by L/L split and the light cycle oil was recycled up to 8 times to prove steady-state quality of the recycle oil and the biocrude product.\[67\]

### 4.3. Char withdrawal

Most of the liquefaction processes eventually produce char suspended in solvent and biocrude. Eventually, the char needs to be withdrawn and the entrapped solvent to be recovered, for example, for recycling. This operation may appear simple at laboratory scale in batch mode; it may nevertheless present operational challenges and costs when performed in continuous operation at larger scale. It may, for instance, require centrifugation/filtration equipment, washing/drying, and, on the way, may lead to equipment fouling. Robust and inexpensive approaches to char withdrawal may be desirable, if not critical, to the operational and economic feasibility of liquefaction processes.

### 4.4. Summary

Biomass feeding may represent the largest engineering challenge for commercializing liquefaction processes. Engineering progress is needed here. Solvent/biocrude recovery can be carried out in various ways and, occasionally, can even be omitted. These concepts still need demonstration at scale, however. Finally, new, robust, and inexpensive approaches to char with-
drawal may still be needed for continuous large-scale operation.

5. Process Concepts

A number of process concepts have been proposed and demonstrated at varying scales. They vary in the choice of solvent, optional use of catalysts, and operating pressure.

5.1. Liquefaction in biocrude

As discussed above, phenolic components are excellent solvents for thermal liquefaction. This opens the option of liquefying lignocellulose in the phenolic biocrude itself. Earlier study revealed, however, that the biocrude is not fully stable and undergoes excessive condensation to heavy products upon multiple recycling.\(^{[76]}\) This leads to a significant increase in biocrude viscosity and, eventually, improper operation.

A solution to this challenge has been proposed by separating the light phenolic fraction from the heavy one using L/L extraction with a very polar or a very apolar solvent and T-swing solvent regeneration (see Section 4.2). The concept was proven by applying multiple solvent recovery and recycling and eventually reaching a steady-state operation after 5 cycles.\(^{[76]}\) The steady state was characterized by a steady biocrude yield close to 90 C% and steady-state biocrude quality (e.g., C:H:O, FTIR, MCRT, vacuum residue fraction). A conceptual process scheme was developed using Aspen HYSYS and a preliminary economic evaluation indicated an overall production cost of $12 per GJ or $54 per barrel of oil equivalent (BOE).\(^{[76]}\)

5.2. Liquefaction in refinery streams

Aromatic refinery streams have also been identified as promising liquefaction media. These streams are affordable and lead to moderate operating pressure when using high-boiling solvent. However, they also deliver a lower biocrude yield than the liquefaction in light biocrude discussed above. Two process schemes have been proposed: once-through liquefaction in VGO and recycle liquefaction in light cycle oil (LCO).

The once-through concept was based on the recognition that VGO is a standard feed for FCC and hydrocracking. Using fresh VGO as liquefaction solvent would result in loading it with a modest fraction of biocrude that may allow straight feeding into an FCC or hydrocracking unit, avoiding thereby the need for solvent recovery and recycle. The liquefaction in VGO was demonstrated experimentally to deliver a biocrude yield of 58 C%.\(^{[93]}\) A conceptual process concept was developed using Aspen HYSYS and a preliminary economic evaluation indicated the possibility to produce biocrude at a cost of $14 per GJ or $54 per BOE.\(^{[93]}\) Conoco Phillips also reported the liquefaction of lignocellulose in VGO at 320–400 °C to produce biocrude with ~60 wt % yield.\(^{[94]}\)

Alternatively, biocrude can be produced by liquefaction in LCO in recycle mode. LCO is an inert stream in FCC operation, hence the need to recover it from the biocrude for recycling to the liquefaction reactor. The LCO can then be recovered from the biocrude by spontaneous L/L split at ambient temperature. The concept was proven experimentally to deliver a biocrude yield of around 55–60% over 8 cycles of liquefaction, biocrude recovery by L/L split and LCO recycle.\(^{[87]}\) Steady state was achieved after four cycles. A conceptual process concept was developed using Aspen HYSYS and a preliminary economic evaluation indicated the possibility to produce biocrude at a cost of $14 per GJ or $54 per BOE.\(^{[87]}\)

Catchlight Energy, a (former?) joint venture between Chevron and Weyerhaeuser, proposed to combine hydrocarbons and oxygenates as solvent for liquefying wood.\(^{[42]}\) The process operates at >250 °C and >14 bar in absence of H₂ and CO. Addition of catalysts such as ZSM-5 reduces the production of heavy product (>5000 Da). Operation at 400 °C and 40 bar results in oil yields of ~70 C% and ~20 wt % oxygen content, with gas and char yields of 15–20 C% and 10–15 C%, respectively. The Catchlight development was won down in 2013, but eventually resumed in a collaboration between Chevron and the Idaho State’s BioCentury Research Farm.\(^{[95–97]}\)

The research is carried out at a scale of 0.5–1 kg h⁻¹ biomass and 2–4 kg h⁻¹ solvent. Bio-oil is produced at 55 wt % yield with hydrocarbon solvents and 67 wt % with phenolic solvents.

5.3. Thermal liquefaction at atmospheric pressure

In another approach, the liquefaction is carried out at atmospheric pressure in a very heavy solvent to allow direct evaporation of the distillate product from the reactor. This low-pressure approach allows easy biomass feeding, low investment cost and delivers a valuable distillate-range product. However, the product yield remains low.

Willner proposed to liquefy straw at 375 °C in a heavy petroleum oil at 1 bar and products are evaporated from the oil.\(^{[98]}\) Biobased products include 10–20% solid, 35–40% oil and 25–30% water and gas (balance). The oil comes as two phases, one lighter than water and the other heavier. It is rich in phenolics and sugar derivatives. The starting oil is partly cracked, leading to a volatile hydrocarbon oil.

In the BioCrack® process, lignocellulose is liquefied in VGO at around 375 °C and atmospheric pressure.\(^{[99,100]}\) The heaviest fraction is retained in the reactor to function as liquefaction medium, and the vapors form a bio-distillate upon condensation. The BioCrack® process is claimed to deliver a yield of 40 C% of light oil and 39 C% of char. The light bio-oil is then hydrotreated using a conventional CoMo catalyst. The liquefaction process is presently operating at a scale 500–800 t a⁻¹ in Schwechat, Austria.\(^{[99]}\)

5.4. Other liquefaction schemes

Although slightly out of scope, recent progress in alternative liquefaction concepts cannot remain ignored. These include the hydrothermal liquefaction and low-temperature acidic liquefaction and hydroliquefaction.

Hydrothermal liquefaction is reaching commercial stage, thereby defying the high investment costs and the biomass
feeding challenges that are expected from extreme operating pressure and very corrosive medium. The latter, the low-temperature acidic liquefaction and hydroliquefaction, are subject of considerable academic interest. However, studies focus on the valorization of carbohydrates to well-defined intermediates and leave the lignin as true by-product.

Ignite, Canada, has developed the catalytic hydrothermal reactor (Cat-HTR) to convert lignocellulose, waste plastic, or lignite to diesel. The operation severity is claimed to depend on the feedstock. Its subsidiary, Licella, has partnered with the Canadian pulp company Canfor to deploy the technology for lignocellulose upgrading at ≈3 ka⁻¹ scale.¹⁰¹,¹⁰² The process is claimed to operate in subcritical water in the presence of base (e.g., NaOH) and hydrogen-donor agent (Na-formate).¹⁰³ It delivers oxygenated chemicals such as phenols, carboxylic acid and ketones but also a biocrude that can be upgraded to diesel and jet fuel through hydrodeoxygenation.¹⁰⁴

Steeper Energy is also using supercritical water and reporting to produce a biocrude with a yield of ≈45 wt% (or 80% energy efficiency) with an oxygen content of 8–10 wt%.)¹⁰⁵ The “hydrofraction” process is being demonstrated at the scale of ≈200 ta⁻¹ in a demonstration unit that is co-located with the Daishowa Marubeni International Alberta Peace River pulp mill in Canada. The technology is designed to deliver renewable diesel at $140 per BOE or $3.3 per gallon.

Acid-catalyzed liquefaction concepts are also worth mentioning. Alonso et al. proposed a multistep process to digest lignocellulose in a γ-valerolactone/water mixture to produce furfural, levulinic acid, and lignin, precipitate the lignin by water addition, and upgrade the levulinic acid to γ-valerolactone for partial recycling as reaction solvent.¹⁰⁶ This technology is presently being developed by GlucanBio.¹⁰⁷ In a similar approach, Cai et al. used tetrahydrofuran as solvent and regenerated their solvent by conversion of the furfural produced.¹⁰⁸ These concepts are aiming at fractionating the biomass and converting the carbohydrates to well-defined intermediates for further upgrading. The lignin remains then as by-product that needs dedicated upgrading or valorization.

Upon addition of hydrogenation conditions, lignocellulose can be converted to C₅–C₆ alkanes and cycloalkanes. Xia et al. reported indeed the conversion of lignocellulose to 28 wt% alkanes, which corresponds to yields of 50–80 mol% on carbohydrates and 10–30 mol% on lignin.¹⁰⁹ The reaction was run in cyclohexane in the presence of Pt/NbPO₄ catalyst. Alternatively, a broader biocrude was achieved by processing lignocellulose in a mixture of water, a bio-based organic co-solvent (e.g., acetic acid or γ-valerolactone), a strong Bronsted acid (H₂SO₄), and hydrogenation conditions (Pd-based catalysts and 80 bar H₂).¹¹⁰ The biocrude consists of monomeric oxygenates (≈40 wt%), oligomeric oxygenates (≈20 wt%), and tar (≈10 wt%) that tail off at ≈1 kDa. The solvent can be recovered by nanofiltration, with selective permeation of the light products, water, H₂SO₄, and monomeric organics, and retention of the heavier components (>250 Da). Such acidic hydroliquefaction schemes clearly require the recovery of catalyst from biocrude and char to recycle it. Catalyst costs are generally unaffordable for processes that produce <1000 kg of product per kg of catalyst before being disposed of.¹¹¹

5.5. Summary

The different process concepts proposed are largely defined around the choice of the solvent and the challenge/opportunities presented by the solvent–biocrude separation. Particularly attractive process schemes are (A) the use of recycled light biocrude as solvent and (B) the once-through liquefaction in VGO for further processing in FCC or hydrocracker without solvent–biocrude separation, and (C) the atmospheric liquefaction in heavy biocrude residue (Figure 13, Table 2). This sequence fol-

![Figure 13. Promising liquefaction processes—simplified schemes.](image)

### Table 2. Promising liquefaction processes—key performances.

| Scheme | Biocrude yields [%] | Investment per annual feed intake (AFI) [$ per ton AFI] | Production cost [$ per BOE] | Ref. |
|--------|----------------------|--------------------------------------------------------|-----------------------------|------|
| A      | 90                   | 93                                                    | 490                         | 54   | [77] |
| B      | 53                   | 59                                                    | 320                         | 64   | [90] |
| C      | 40                   | –                                                     | –                           | –    | [94] |

[a] LHV = Low heating value. [b] Investment per annual feed intake (AFI).
consumption to an affordable level.\textsuperscript{(62)} This restriction may be less severe for very cheap catalysts such as “red mud” mentioned earlier in Table 1.

Despite the tentative ranking in process attractiveness proposed above, one should recognize that the most advanced technology is none of these. It is a hydrothermal liquefaction (Licella and Steeper Energy), which has so far been qualified here as challenging because of its high investment cost. The future will tell us which is eventually the winning liquefaction technology.

6. Conclusions and Perspective

The liquefaction of lignocellulose to biocrude and subsequent refining to biofuels are no new concepts. Liquefaction was subject of intensive research after the oil crises in the 1970ies and regained interest at the turn of the 21\textsuperscript{st} century. Much understanding has been gained, for example, on the chemistry of the process, the chemical characteristics and properties of the biocrude, the impact of the solvent, and the role of optional catalysts on the process. Several process schemes have been proposed to maximize biocrude yields, minimize solvent cost and, eventually, minimize manufacturing cost.

Research has also been devoted to using the biocrude as boiler fuel or heavy duty fuel. Research has also looked at biocrude upgrading to light transportation fuels by means of FCC or hydrocracking/ hydrodeoxygenation. Several concepts have been pushed to demonstration scale; one of them is now moving to (small) commercial scale of 3 kt a\textsuperscript{-1} by Licella/Canfor. Nevertheless, numerous challenges remain to increase the chances of commercialization.

The first and most important one is probably the proper valorization of the biocrude product. The upgrading to light biofuels still suffers from modest yields and significant cost. Valorization as material might offer better promises.

A second important challenge is low-cost feeding of the biomass, particularly when carried out at a large scale, for example, 500 kt a\textsuperscript{-1} intake. The combination of high temperature, significant pressure, change from “dry” to “wet” environment, and characteristics of the biomass (e.g., low density) present significant engineering challenges.

Various concepts have been put forward to separate the biocrude from the solvent. Demonstration at scale is still needed.

Finally, the field of liquefaction still offers a wealth of scientific challenges to be solved and understood. These vary from detailed understanding of the depolymerization chemistry to the effect of solvent and catalysts and in-depth characterization of the biocrude through hybrid spectroscopic methods.

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Conflict of interest

The authors declare no conflict of interest.

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