



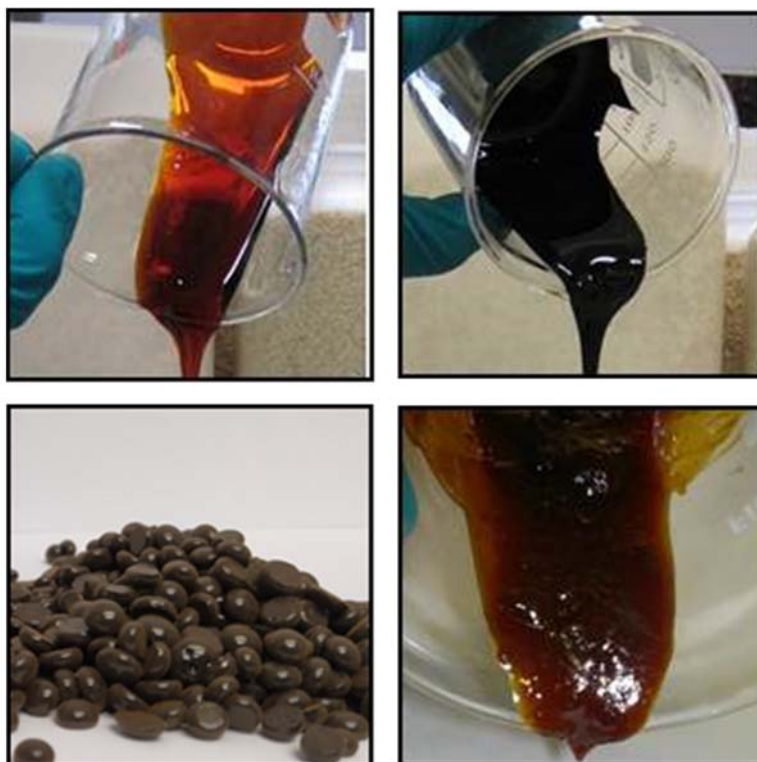
IEA Bioenergy
Technology Collaboration Programme

Production of Chemicals and Materials from Direct Thermochemical Liquefaction

Potential applications, status, outlook and challenges

IEA Bioenergy: Task 34

January 2024





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Production of Chemicals and Materials from Direct Thermochemical Liquefaction

Potential applications, status, outlook and challenges

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Introduction

The burgeoning demand for energy and materials, coupled with the imperative to reduce greenhouse gas emissions, has amplified the focus on sustainable bio-resources like biomass. Biomass, being a renewable and abundant resource, holds promise for the production of fuels, chemicals, and materials in a sustainable manner. Two prominent direct thermochemical liquefaction technologies, Pyrolysis and Hydrothermal Liquefaction (HTL), are pivotal in unlocking the potential of biomass. This report delineates the principles, potential, and challenges inherent to these technologies, along with the outlook for deriving valuable products. The discourse commences with an exploration of Pyrolysis, elucidating the opportunities for deriving chemicals from fast pyrolysis bio-oil, followed by a segment on Hydrothermal Liquefaction, emphasizing the utilization of components from the aqueous phase. The narrative culminates with a summative outlook, drawing parallels and distinctions between the technologies, and exploring research needs to advance the technology.

Introduction to Pyrolysis

Pyrolysis is the thermal decomposition of a material under inert conditions. Biomass pyrolysis results in the formation of solid, liquid, and gaseous products. When it is desired to maximize the liquid product, fast pyrolysis is applied. The term *fast* refers to the heating rate, which is in the order of magnitude of 100-1000 °C/s. Typically, temperatures around 500°C are applied, and to maximize the liquid production rapid condensation of the vapours is required. Fast pyrolysis has an overall energetic efficiency of around 90% (including Fast Pyrolysis Bio Oil, process steam & electricity generation) and for clean woody biomass (e.g. pine wood) up to 70 wt.% of a liquid product can be obtained. About 15 wt.% of the biomass is converted into charcoal and the remaining 15 wt.% to non-condensable gases. Importantly, the minerals present in the biomass are not, or only minimally transferred into the oil. The ashes (minerals) are readily collected from the process and can be re-used (e.g. fertilizers). Depending on the technology applied, the charcoal product and non-condensable gasses can be burned to cover the internal energy demand, excess of energy can be used to produce steam and/or electricity for heat and power applications (e.g. fractionation and further processing). The obtained liquid is polar, acidic and it contains water (~23 wt%) as an integral part. The liquid is a mixture of depolymerized (partly cracked) components derived from cellulose, hemicellulose, lignin and resin material (fatty acids, terpenes, etc.). Cellulose and hemicellulose are converted to sugar monomers, oligomers and polymeric fractions often in the anhydro form and into smaller carbonyls, acids and water. The lignin is converted into monomeric-, oligomeric- and polymeric lignin derived components. Importantly here is that due to the very short heating times, the cellulosic sugars and lignin are mainly depolymerized and only minimal cracked hereby thus largely retaining their chemical functionality. The resin material is also only partly depolymerized in pyrolysis, and depending on the feedstock used is sometimes found as a hydrophobic layer on the pyrolysis oil. A lot of research has been performed world-wide on the conversion of various residue streams by fast pyrolysis using a large number of reactor configurations. In the case herbaceous biomass streams such as grasses and straw are directly used in the fast pyrolysis process lower liquid yields are obtained, typically yielding 55-65 wt% of liquid, and the char production increases significantly. The presence of mineral matter in the biomass is one of the dominating parameters in the product distribution. Fast pyrolysis of biomass is performed on a commercial scale, the annual production capacity is > 150 kt¹. In Europe, commercial sized fast pyrolysis plants (> 10 MWth) are operational Lieksa, Finland (GreenFuelNordic), in Gävle, Sweden (Pyrocell) and in Hengelo, the Netherlands (Empyro). These 3 plants are using the rotating cone fast pyrolysis technology. Furthermore, outside Europe two commercial

pyrolysis plants can be found in Canada and five in the U.S., all of which are based on the RTP® technology from Ensyn.

Introduction to Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is a thermochemical conversion process that converts wet biomass (e.g., algae, sewage sludge, wood, food waste, organic wastes), into a high-energy-density liquid fuel under high temperature (typically 250°C to 400°C) and pressure (up to 25 MPa)²⁻⁶. In the liquefaction, the organic content of wet biomass is liquefied, producing a biocrude, a dilute aqueous phase, and a solid residue, which is rich in carbon and minerals. The biocrude, which contains high amounts of oxygen and nitrogen, can be hydrotreated, to produce diesel, gasoline, jet fuel, and other products^{7, 8}.

An advantage of HTL is its ability to process wet biomass, reducing the extent of dewatering or drying required, which can be energy-intensive and costly. Some challenges associated with the process include the combination of high-temperature and high-pressure required in these processes and fouling of the equipment. Still HTL has potential as a promising technology to convert wet biomass into liquid fuels and other valuable products. HTL can process a variety of feedstocks, including those with varying chemical compositions, and physical properties. Generally, any biomass with high organic matter can be processed in HTL, albeit with varying levels of biocrude quality and/or yield. The main HTL feedstocks include: (a) Algae (high lipid content), (b) Sewage sludge, a byproduct of wastewater treatment, (c) Forestry residues, such as wood chips and sawdust (high lignocellulosic content), (d) Agricultural residues, such as corn stover and wheat straw, can also be used as a feedstock for HTL (high cellulose and hemicellulose content), (e) Manure and (f) Municipal solid waste. Feedstock selection depends on various factors, including availability, cost, inorganic ash content, chemical composition of the biomass, and the quality and yield of biocrude³.

The main product from HTL, biocrude is traditionally used to produce liquid transportation fuels. Still, potential applications for materials and chemical applications are being explored as described here.

In general, the HTL process undergoes a complex variety of depolymerization, decomposition, and recombination reactions⁹. Due to the variety of chemical reactions possible, HTL biocrude consists of a very wide range of different chemical species and functionalities. Further, HTL biocrude composition varies depending on the feedstock type and composition, and the processing conditions.

The general molecule types in HTL biocrude include (a) monoaromatics such as phenol, benzene, styrene, and toluene, (b) polyaromatics such as naphthalene, quinoline, indene, anthracene, phenanthrene, pyrene, and fluorine, (c) fatty acids like myristic acid, palmitic acid, steric acid, oleic acid, myristic acid, octanoic acid, and hexadecenoic acid, (d) alkanes, alkenes and cycloalkanes, and (e) oxygenated and/or nitrogenated compounds. Feedstock classes drastically influence the biocrude composition^{10, 11}. Wood and cellulosic materials produce more phenolics, aromatics and cyclic compounds due to the cyclic nature of lignin and cellulose. Organic wet wastes and algae tend to have more nitrogenates (due to the protein content of the feed) acids and esters^{2, 10, 12, 13}.

The oxygenated compounds in biocrudes are formed as a result of the depolymerization of carbohydrates, proteins, and lipids in the biomass^{10, 14}. Oxygenated compounds include (a) carboxylic acids, which can be formed through the dehydration and decarboxylation, (b)

aldehydes (can be formed via dehydration and dehydrogenation), (c) ketones (can be formed via dehydration and dehydrogenation), (d) esters (esterification of carboxylic acids and alcohols), and (e) phenols (depolymerization and decomposition of lignin and aromatics). The oxygenated component can influence the biocrude properties. In addition to oxygenates, biocrude contain nitrogen-containing compounds (primarily from proteins), sulfur-containing compounds, and trace amounts of inorganics, including, sodium, potassium, iron, silica, calcium, and magnesium. These impurities may require further processing to meet the desired specifications for subsequent upgrading steps such as hydroprocessing^{8, 15}.

The nitrogen-containing compounds in the biocrude can be problematic for fuel production and can potentially contribute to emissions of nitrogen oxides (NOx) during combustion^{16, 17}. The nitrogen content in biocrude from HTL can vary depending on the type of feedstock and process conditions, but it is generally higher than in conventional petroleum crude oil. The nitrogen in the feedstock (primarily from proteins) is converted into various nitrogen-containing compounds during HTL, including pyrazines, pyrroles, pyridines, pyrrolidines, indoles, and amines⁷. This can make it more challenging to upgrade biocrude into high-quality transportation fuels.

Overall, the composition of biocrude is complex and varies depending on the feedstock and processing conditions. However, with proper analysis and processing, biocrude can be a valuable source of renewable energy and chemicals.

Literature survey of proposed chemical and material opportunities for pyrolysis bio-oil and biocrude

PYROLYSIS BIO-OIL PATHWAYS AND FRACTIONATION ALTERNATIVES

The utilisation of pyrolysis oil as energy carrier to substitute natural gas or fuel oil is proven technology^{1, 18}. However, to fully utilize the potential of pyrolysis oil, it is desired to make optimal use of the chemical structure of the pyrolysis oil¹⁹. Since biomass is the only source of renewable carbon, the substitution of chemicals and materials currently produced from fossil resources by biomass derived products is highly desirable. Pyrolysis oil is a mixture of hundreds of components, derived from the thermal decomposition of the original biomass. The components contain different chemical functional groups such as lignin/phenolics, acids, sugars, etc. While extraction of pure components is challenging due to the low concentrations of individual components and the number of required steps to obtain that specific component, obtaining fractions with similar functionalities or boiling point ranges is relatively easy. Also, FPBO is a suitable commodity for other conversion processes to yield a variety of valuable chemicals.

Production of chemicals from fast pyrolysis bio-oil via other conversion processes

The application of fast pyrolysis to produce several food ingredients, primarily smoke/ grill flavour, has been realized as commercial process for decades; primarily in the U.S. by Red Arrow (part of the Kerry Group). These units have been provided by Ensyn and are based on their Rapid Thermal Processing technology²⁰. This application is not limited to fast pyrolysis, similar food ingredients are also produced from slow pyrolysis and available on the market²¹.

With the demonstration project in Preem refinery, the use of bio-oil as co-feed (<3%) in a fluid catalytic cracker of existing petroleum refineries is the application which is currently closest to reach market implementation²². This opens up the opportunity to produce classical

petroleum refinery chemicals and enter existing markets; however, only as share of renewable carbon in otherwise fossil based products. The amount of co-feeding is limited but represents a short-term alternative that can be ramped up rapidly. The share of FPBO can be increased through adding an upgrading step for the removal of oxygen (functionalities).

FPBO can also be used as feedstock for gasification to produce a syngas and consequently open up the product spectrum available from Fischer-Tropsch or other synthesis pathways¹. Gasification of FPBO with subsequent synthesis of dimethylether (BioDME) has been demonstrated at TRL 6 in entrained flow gasifiers with a thermal capacity of 3 and 5 MW^{23,24}.

FPBO (or fractions thereof) can also be used as feedstock for microbial conversion²⁵, opening up yet another range of chemicals available via such pathways²⁶⁻²⁸. There have been some promising results reported at low TRL to overcome the challenge of many substances that potentially inhibit microbial activity²⁹⁻³⁹. While implementation at scale has not been realized as of today, this indirect pathway towards valuable chemicals should be further investigated.

Regarding the production of pure compounds, catalytic pyrolysis appears as a promising way to increase the selectivity of specific chemicals. The catalyst can be placed either in the pyrolysis reactor (in-situ) or in a downstream reactor to selectively convert the pyrolysis volatiles (ex-situ). A well selected catalyst can enhance a specific pathway, resulting in a bio-oil with higher content of some compounds of interest. An illustration is the Cyrene™ process, where the cellulose component is converted into levoglucosenone (LGO) through a highly selective catalytic process. LGO is then converted in one step into dihydrolevoglucosenone, which can be obtained with a purity of 99%. Dihydrolevoglucosenone, trademarked as Cyrene, is an environmentally friendly alternative to solvents such as dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAc). In the context of the Resolute project, the first of its kind industrial plant is currently under development with the objective to be operational in 2024.

Fractionation of pyrolysis oil by staged condensation

Fractionation of pyrolysis oil by staged condensation is often proposed in literature⁴⁰⁻⁴². Fractions are produced by applying several condensers set at different temperatures. Separation of fractions is thus obtained on the basis of boiling point/vapor pressure and not on solubility in specific solvents, which in contrast allows to separate on basis of chemical functionalities⁴³. Staged fractionation has been applied at pilot scale between at 8 and 500 kg h⁻¹ feed capacity since 2009 with different approaches^{44, 45}.

In most cases, staged condensation is applied to produce an organic rich oil fraction and, at lower temperature, an aqueous condensate. With a carefully chosen temperature, the organic rich oil fraction is FPBO according to current standards and registration files. Some studies apply higher condensation temperatures than in commercial processes, which leads to an organic rich fraction with different quality than the currently traded FPBO commodity, e.g. a lower water content, higher heating value and higher viscosity. The design of the higher first condensation temperature is typically matched to optimize simultaneous valorization of the aqueous condensate recovered in the second stage. This aqueous condensate is not a mandatory by-product of fast pyrolysis. Current commercial installations

¹ Gasification of Liquids derived from Direct Thermochemical Liquefaction, available at: <https://task34.ieabioenergy.com/dtl-oil-gasification-2/>

for the production of FPBO avoid condensation of this fraction and combust it within the process to produce heat. The aqueous condensate produced by staged condensation contains similar chemicals as discussed later for the aqueous fraction of the extraction process.

Fractionation of pyrolysis oil by liquid/liquid extraction

Pyrolysis oil can readily be fractionated by liquid/liquid extraction into three main fractions, being:

1. Pyrolytic sugar syrup (~45% of the original carbon)
2. Pyrolytic lignin (~35% of the original carbon)
3. Extractives

Each of the fractions can be a starting point for further processing into the green chemicals and products. The fractionation process starts with a fractionator, using an aqueous solution as the extraction agent, in this way the lignin fraction is separated. In the second step a sugar syrup is obtained by removing water by evaporation, co-producing an aqueous fraction containing small organic components like acetic acid in water. Depending on the application or subsequent downstream processing the fractions can be further upgraded or purified. Prior to the fractionation, extractives may be removed in a separate extraction step. The fractionation of FPBO to obtain the sugar, lignin and optionally extractive streams has been subject of development work for about 10-15 years in the Netherlands at BTG and in the U.S. at Iowa State University⁴⁶. Currently a pilot plant (120-125 kg/h) is operated in the Netherlands (BTG) for the fractionation of FPBO's. The core of the fractionation process is based on liquid-liquid extraction in which both extractants are recovered, and recycled within the process.

PYROLYTIC SUGAR

Pyrolytic sugar (PS) can be isolated in amounts up to 30-35 wt% of the original oil, as a water free highly viscous syrup. It is a broad mixture of various sugar derived components such as glycolaldehyde (>12 wt%), levoglucosan (>18 %), glucose and sugar -oligomers and -polymers and a small amount of water-soluble lignin fractions. With pretreatment and/ or suitable additives, sugar yield can be significantly increased⁴⁶. Sugars obtained from pyrolysis oil are mainly of the C₆ form and are partly present in the anhydro form. The sugars are soluble in many solvents, mineral free and have a very high potential to serve as a renewable source for a broad range of chemo-catalytic transformations such as in: hydrolysis, isomerization, dehydration, hydrogenolysis, and retro-aldol condensation. The levoglucosan, discussed as potential platform molecules in itself⁴⁷, cellobiosan and other sugars in the pyrolytic sugar fractions can be hydrolysed to produce high amounts of monomeric sugars like e.g. glucose, manose, xylose etc. Subsequently these monomeric sugars can be converted into ethanol by fermentation or into base/platform chemicals such as furfural, HMF, levulinic acid and formic acid by acid catalysed dehydration & hydrolysis of the sugars. In the finalised EU funded project Bio4Products, it was already demonstrated that the PS could be used in various products such as in moulding resins and in wood preservation formulations, replacing a.o. fossil and toxic creosote⁴⁸. In the EU project NewWave, the PS will be used to produce HMF, a platform chemical which can be used in furan chemistry and as a replacement for formaldehyde in f.i. resin applications. Also, the PS will be used to make polyols, applied/explored as solvents and in PUR applications⁴⁹. The potential for the PS could be enormous, various platform chemicals could theoretically be produced from it. Glycolaldehyde f.i. has an enormous potential to become a bio-based C₂ platform chemical according to Faveere *et al.* e.g., as a bio-derived alternative for ethylene oxide via the production of bio- ethylene glycol⁵⁰. The pyrolytic sugar is registered in CAS under number 2414605-13-1, and a REACH dossier has been filed for an annual production of 10 ton.

PYROLYSIS AQUEOUS FRACTION

The aqueous fraction obtained by staged condensation at low temperatures, water removal from pyrolysis oil by evaporation, or in the production of the pyrolytic sugar syrup contains hydrophilic low-molecular and low-boiling components such as acetic acid, methanol, furfural, hydroxyacetone, and small amounts of monophenols. These aqueous fractions show some similarities with wood vinegar and could be used as a green pesticide/herbicide (a biocide). From literature it is known that e.g. wood vinegar and pyrolysis derived liquids are potentially promising biocides² or fertilizers depending on the concentration of the present components. Furthermore, organic acids could be retrieved from these fractions by applying various separation techniques or by converting them to calcium/magnesium salts (CMA/MCA), which can be used as de-icers.

PYROLYTIC LIGNIN

Pyrolytic lignin (PL) can be isolated in amounts up to 25-30 wt% of the original oil, as a highly viscous liquid. It is a mixture of depolymerised lignin fragments, some water and small organics. The PL is mineral free, and easily further processed to obtain a solid PL. Since PL is partly depolymerized, and it is not contaminated by external chemicals as for example kraft-lignin it is very suitable to be used in different applications. Currently the most advantaged application of the pyrolytic lignin is in the replacement of fossil phenol in different resins systems^{48, 49}. These resins are a.o. used to produce insulation foams which has already been demonstrated in EU funded project Bio4Products on a relevant pilot-scale. Furthermore, the PL could be used as phenolic source to produce monomers, BTX and other platform chemicals having a phenolic or aromatic functionality or as an active ingredient in the production of bio-based paints, coatings, and binders. The pyrolytic liquid is registered in CAS under number 2411004-28-7, and a REACH dossier has been filed for an annual production of 10 ton. The solid pyrolytic lignin is registered under number 2411004-20-9.

PYROLYTIC EXTRACTIVES

Depending on its nature, wood can contain up to 5 wt% of resin (also called pitch or extractives) material and f.i pine needles even up to 13 wt%. Typically, wood resin is non-polar or lipophilic and therefore doesn't dissolve well in water. Wood resin consists of many different components such as fatty acids, waxes, rosin acids, terpenes and many more. As for the lignin and cellulose/hemi-cellulose it is assumed that the resin components are slightly cracked/depolymerized but largely retain their chemical functionality in fast pyrolysis. This was also observed by Oasmaa *et al*, who investigated the effect of extractives on the phase separation of pyrolysis oil⁵¹. For the pyrolytic lignin and sugar multiple applications have been identified. But for the extractives this is not yet explored to a large extent yet. Nowadays wood resins are considered as a bio based (platform) material for all kinds of specialty chemicals (Pine chemicals) and as a source to produce tall oil fuels. The extractives show some similarities with tall oils and could therefore possibly be used in comparable applications.

² K. Tiilikkala, L. Fagernäs and J Tiilikkala, Open Agr. J., 2010, 4, 111-118

HTL BIOCRUDE

Fractional distillation has been explored as a means to separate and refine the components of biocrude produced from HTL because biocrude typically contains a wide range of compounds with different boiling points.¹³ Fractional distillation is a common technique used in the refining of crude oil to separate the different hydrocarbon fractions based on their boiling points. During fractional distillation, the biocrude is heated, and the resulting vapor is condensed and collected in different fractions, each containing compounds with a similar boiling point range.

The separation of biocrude through fractional distillation can be challenging compared to petroleum crude oil, because biocrude contains a higher proportion of polar and oxygenated compounds which increase the boiling point of the biocrude. This requires higher distillation temperatures which can lead to cracking of the biocrude and potentially lead to fouling and corrosion of the distillation equipment.

Overall, while fractional distillation can be used on HTL biocrude, it may require modifications to the process and equipment to account for the differences in the chemical composition compared to conventional crude oil. Additionally, other conversion processes, such as hydrotreating or hydrocracking, may also be necessary to upgrade biocrude into high-quality transportation fuels.

HTL AQUEOUS PHASE

The HTL aqueous phase (HTL-AP) has been identified as an opportunity for further carbon recovery, but it also represents a major liability for the HTL process. For wood and other dry feedstocks, the HTL-AP can be recycled in the process to the headworks of a HTL facility, thereby improving the overall biocrude yield^{12, 52, 53}. However, wet feedstocks such as sewage sludge, manure, or food waste cannot be economically recycled to the headworks of a HTL facility without over-diluting the feedstock^{54, 55}. Further, the HTL-AP can not always be recycled to the headworks of a water resource recovery facility (WRRF) due to challenges associated with increasing the nitrogen load on the plant, adding toxic components⁵⁴ to the feedstock, and potentially hindering the ultraviolet (UV) disinfection process of the treatment facility. While the HTL-AP is rich in organics, a key challenge with extracting components from the HTL-AP is the dilute nature and complexity of the stream. HTL of wet wastes, such as sewage sludge, manure, or food wastes, produces a complex mixture of organic species, many of which are not high value species. Part of the challenge in upgrading this stream is that it consists of a mix of many low-molecular-weight and low-value components. Depending on the waste stream, the HTL-AP can contain carboxylic acids (mainly acetic acid and propanoic acid), ethanol, acetone, and glycerol. However, the low total organic content (2-3% carbon) in the HTL-AP makes separation challenging. Figure 1 breaks down example HTL-AP compositions from three continuous HTL runs in a "Sherwood plot". The Sherwood line is a quick way to identify if purification of individual components is likely economically viable. The analysis is not favourable for purification of individual chemicals for the HTL-AP. This highlights the need for a low capital, low operational cost conversion or treatment strategy.

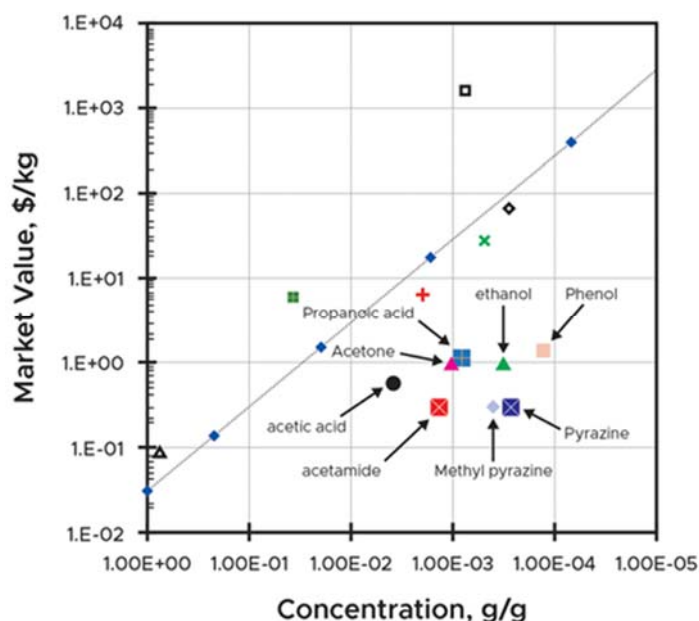


Figure 1. Sherwood plot demonstrating the value of HTL aqueous phase composition.

A comprehensive review for valorization of the HTL-AP was published by Watson et al. in 2020⁵⁶. Briefer and more recent reviews have also been published by SundarRajan et al. and Swetha et al. in 2021^{57, 58}. The review published herein summarizes several findings from Watson et al. and SundarRajan et al. and includes updates since their publication. In general, the main approaches to obtain chemicals from the HTL-AP include separation, biomass cultivation, anaerobic fermentation, bioelectrochemical systems, hydrothermal gasification, and recycling for HTL. The advantages and challenges of each of these approaches are summarized in Figure 2.

Thermochemical Conversion

Direct conversion of the HTL-AP to fuel gases (e.g. hydrogen or methane) via thermochemical processing is also possible. Catalytic hydrothermal gasification (CHG) is a process to treat HTL-AP. CHG converts organic compounds in the HTL-AP to basic gases such as hydrogen, methane, carbon dioxide, and carbon monoxide with the use of a catalyst at high temperature and pressure. The advantage of using a catalyst in CHG, is that it can be operated in the condensed phase, thereby reducing the extent of water which must be vaporized. The selectivity of the product gases can be varied by the reaction temperature. There are competing reactions that can occur. Advantages of CHG including (a) converting the organic compounds in the waste stream into a useful gas that can be used for energy production, and (b) significantly reducing the volume of waste by converting the organic compounds into gas, which can be easier to store and transport than a liquid waste stream.

Heterogeneous catalysts, typically Ni and Ru, have been shown to be the most effective at improving the conversion rates in CHG applications⁵⁹⁻⁶¹. Thermal stability of the catalysts in the hydrothermal environment are still a concern. Catalyst poisoning, mainly due sulfur, is another common challenge. Sulfur removal is possible with pre-treatment or the use of a guard bed to preserve the lifetime of the CHG catalyst. Additionally, the gas generated from CHG may require further processing to remove impurities and increase its quality, which can add to the cost of the process.

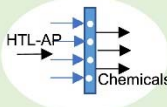
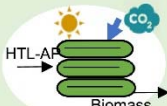


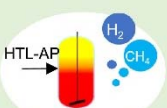
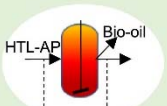
Approaches	Advantages	Challenges
 <p>Separation Chemicals are separated and concentrated from HTL-AP through nanofiltration and resins</p>	<ul style="list-style-type: none"> Value-added chemical extracted No chemicals added Operated under mild conditions 	<ul style="list-style-type: none"> Energetically taxing Needs economic evaluation Residual organics in HTL-AP remain Unsuitable for HTL-AP with complicated composition
 <p>Biomass cultivation Algae, microbes, and/or crops are grown using nutrients and organics in HTL-AP and carbon is captured by biomass</p>	<ul style="list-style-type: none"> Biomass could be utilized for food and biofuels production Nutrients are efficiently utilized 	<ul style="list-style-type: none"> Heavy dilution is required Limited organics conversion Large land area requirement Risk of heavy metals accumulation
 <p>Anaerobic fermentation Organics in HTL-AP are converted into hydrogen and methane by microbes in a fermentation reactor</p>	<ul style="list-style-type: none"> Efficient organics conversion Energetically positive due to production of energy gas Low sludge production Low operating cost 	<ul style="list-style-type: none"> Dilution is required Limited nutrients removal Long retention time Large land area requirement
 <p>Bioelectrochemical systems Electricity or hydrogen is produced from HTL-AP, and organics are mineralized</p>	<ul style="list-style-type: none"> Efficient organics conversion Energetically positive due to hydrogen or electricity production Low sludge production 	<ul style="list-style-type: none"> Dilution is required Limited nutrients removal High reactor cost Needs economic evaluation
 <p>Hydrothermal gasification Hydrogen-rich gas is produced from HTL-AP at >400°C and organics are mineralized</p>	<ul style="list-style-type: none"> Efficient organics conversion Fast conversion process Energy gas produced No dilution required 	<ul style="list-style-type: none"> High requirement for reactor Operated at high temperatures and pressures Catalysts are required Limited nutrients removal
 <p>Recycle for HTL HTL-AP is recycled to HTL reactor to serve as a solvent and reactant</p>	<ul style="list-style-type: none"> Biocrude oil yield is enhanced Fast conversion process No dilution required No additional reactor needed 	<ul style="list-style-type: none"> Needs economic evaluation Only a fraction of the HTL-AP is treated Concentration of organics is increased in residue effluent

Figure 2. Comparison of the state of technology of different HTL aqueous phase valorization approaches. The advantages and limitation are evaluated based on the findings of previous studies. Reprinted from *Progress in Energy and Combustion Science*, Vol 77, Watson et al., *Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability*, 100819, Copyright 2020, with permission from Elsevier.

Steam reformation of hydrocarbons and water-gas shift can yield hydrogen at relatively lower temperatures (300 - 600 °C). At higher temperatures (>600 °C) methanation can occur, reducing the hydrogen yield^{56, 62}.

Homogenous catalysts, typically alkali solutions, can promote the water gas shift reaction, favoring the production of hydrogen. However the dissolved catalyst is difficult to recover and can produce other impurities (e.g., carbonates and formates)⁵⁶.

In some instances, the indirect conversion of the HTL AP is demonstrated by using it as a recycled medium for HTL. In the cases of feedstocks with insufficient water content for HTL, such as dried lignocellulosic or woody biomass, water is added for the HTL reaction. When the HTL AP is reused, it can facilitate additional recovery of the carbon by its incorporation into the final fuel products⁵²⁻⁵⁵.

Nutrient Recovery for Biomass Production

The HTL AP is typically rich in nutrients valuable for cultivation of terrestrial and aquatic biomass⁶³. For example, nitrogen and phosphorus are typically retained in the HTL AP. Metal micronutrients such as potassium, magnesium, iron, and zinc are also recoverable^{64, 65}. The

reuse or sale of the nutrients enables environmentally and economically sustainable conversion via HTL.

Direct recovery of the nitrogen is possible through air stripping, membrane separation, and adsorption⁶⁶. The majority of the nitrogen in the HTL AP is in the form of ammonia. Sparging the AP with air can remove the ammonia, which can then be scrubbed by adsorption into an acidic solution. The recovery of nitrogen via ammonia is effective but does not capture all of the available nitrogen as some is in the form of heterocyclic compounds such as pyridines, pyridines, amides, amines. Additional treatment is needed to remove or convert organic nitrogen for recovery. Ammonia in the HTL-AP can also be driven out as ammonia gas via the addition of calcium carbonate or calcium oxide (quicklime) and the resulting ammonia recovered via adsorption.

Struvite precipitation is another common process to utilize available nitrogen, phosphorus, and magnesium in the HTL AP⁶⁷⁻⁷⁰. Struvite is a valuable fertilizer product that is currently marketable. Struvite can form naturally in the HTL-AP but has to be precipitated and purified for sale. This is an emerging area for HTL-AP but with significant interest because of the value that can be recovered from the struvite⁷⁰.

Another proposed approach for nutrient recovery is electrodialysis, which is a membrane-based process that can be used to recover nutrients from the HTL-AP. In this process, the HTL-AP is passed through a series of ion exchange membranes, which selectively remove ions, such as nitrogen and phosphorus, from the stream. The ions can be collected and concentrated, and further processed into solid or liquid fertilizer products.

In the context of an algal biorefinery, algae are cultivated, harvested, and then hydrothermally process to produce fuels and other products. Significant material costs are associated with the nutrients, specifically nitrogen and phosphorus that are required for cultivation. In an ideal biorefinery, the nitrogen and phosphorus are recovered and reused in cultivation. Although a majority of the nitrogen is recovered in the HTL-AP as ammonia, the concentration may be too high for direct feeding (i.e., without dilution)⁷¹. Although some micronutrients remain soluble in the HTL-AP, it is not always the case, and they have to be recovered from the HTL solid products or supplemented in a cultivation system. Additional details are in the following section.

Pre-treatment and Biological Conversion

Another potential use of the HTL-AP is as a substrate for biological processes. The HTL-AP may be the primary substrate or a supplemental secondary substrate. Each potential conversion pathway has a distinct purpose, such as: 1) recycling the HTL-AP as substrate to produce the original HTL feedstock (i.e., direct nutrient recovery); 2) cultivating additional HTL feedstock, usually a microorganism, to boost HTL feedstock quantity; and 3) upgrading the HTL-AP via biological conversion to fuels or other products.

Regardless of the conversion pathway, the HTL-AP can be difficult to degrade or convert biologically. Toxins or toxic concentrations of substrate components can inhibit biological activity and metabolism⁷². Recalcitrant materials such as high molecular weight components, aromatics, and nitrogen-containing heterocycles resist degradation. Pre-treatment steps are often included to reduce or remove inherent toxins. The simplest pre-treatment is dilution, which can be successful, but can disrupt the water balance of a process. Although dilution can show immediate success, the long-term accumulation effects of toxic compounds is mostly unstudied. Destructive methods, mainly oxidation treatment, are successful in

reducing the concentration of toxic compounds⁷³. Oxidation methods include ozonation, hydrogen peroxide, and UV light. Thermal destruction can be successful, but the thermal process must be at a higher temperature than the original HTL process that produced the toxic components, that is, hydrothermal gasification is typical to achieve destruction. However, destructive methods are nonselective and can reduce the quality of the substrate by destroying beneficial or valuable components. Depending on the oxidizing agent, biological growth may be inhibited by the agent itself or by by-products of the agent. Removal methods include adsorption or extraction. Common solid adsorbents such as zeolites, activated carbon, and resins have shown positive treatment outcomes of the HTL-AP⁷⁴. However, regeneration can be difficult, so the most preferred method is to determine the lowest cost adsorbent that can be used and then discarded. Liquid-liquid extraction is also possible to remove toxic compounds.

Direct recovery and use of the available nutrients in the HTL-AP creates an opportunity for sustainable development of the HTL process. Microalgae is a commonly used feedstock for HTL. To design a completely sustainable process, the re-use of the HTL-AP in the cultivation process is a priority topic of research. Dilution is the most common pre-treatment for algae utilization of the HTL-AP. Complete reuse of the HTL-AP is possible, however it should be noted that P typically partitions to the solid phase products, therefore it must be extracted from the solids for use in algae cultivation⁶⁵. In successful trials, the HTL-AP is fed back to algae cultivation creating a closed loop process. Long-term effects of continuous HTL-AP recycle is still under investigation and should be considered for robust commercial operations.

In other cases, the HTL-AP is used as a substrate for the cultivation of microorganisms to supplement the HTL feedstock^{75, 76}. Again, dilution is important to prevent growth inhibition and some adaptive evolution of the microorganism occurs to maximize potential. Doing so can boost overall carbon recovery. Alternatively, the HTL-AP can be a substrate for the production of biologically derived platform chemicals.

Anaerobic digestion is another biological process that can convert the carbon in the HTL-AP to biogas, which can be used directly as an energy product, or upgraded and purified to renewable natural gas. Anaerobic digestion technology is commercially available and few modifications are needed to adapt it for utilization of the HTL-AP. Several studies have shown successful integration of HTL-AP into anaerobic digestors, but there are still limitations due to the toxicity concerns mentioned previously⁷⁷⁻⁸¹.

Bioelectrochemical conversion methods⁸¹, using microbial fuel cells or microbial electrolysis cells are also possible methods to produce energy products, in this case electricity, from the HTL-AP. However, this is still an emerging field with limited studies available. In addition to generating electrical energy, microbial electrolysis cells can produce hydrogen gas.

Electrochemical conversion (H₂ or CH₄)

Electrolysis has been explored to produce hydrogen from the HTL-AP. This process uses an anode and a cathode separated by an electrolyte solution with a voltage applied across both electrodes. The total voltage applied across the reactor cell induces chemical reactions at each electrode surface (cathode and anode). Organic compounds act as electron donors, which reduces the overpotential at the cathode to produce hydrogen (as compared to water splitting). However, it is important to carefully select the organic compounds to ensure that they do not interfere with the electrode reactions or the performance of the electrolyzer. Further, the electrodes may be susceptible to catalyst poisoning, thereby hurting the long-term viability of a process.

Insights on the outlook, and challenges

Pyrolysis

Numerous valuable products can be derived from pyrolysis, including purified chemicals from bio-oil, biochar, syngas (via gasification of the bio-oil), and various chemicals with potential applications.

The conversion pathways for deriving chemicals from fast pyrolysis bio-oil include co-feeding with petroleum refineries, gasification to produce syngas, and microbial conversion. With successful scale-up and efficiency improvements, these pathways could offer significant contributions to renewable chemical production. Additionally, the potential to fractionate bio-oil into different valuable fractions via staged condensation or liquid/liquid extraction offers an avenue for producing a range of sustainable chemicals and materials. As these technologies continue to advance, the commercial viability of these methods will likely improve.

HTL

While there are opportunities for producing materials and chemical from HTL biocrude, the area of most research for producing chemicals from HTL lies in valorisation of the carbon content in the aqueous phase. Despite the challenges posed by the complexity and dilute nature of this phase, it contains a significant amount of carbon that can be further processed to produce valuable chemicals and fuels.

The aqueous phase from HTL represents a crucial source of potential value, given that it is a rich mixture of organic and inorganic compounds. Extraction and refinement of these compounds could lead to the production of several valuable chemicals, such as carboxylic acids (like acetic and propanoic acid), ethanol, acetone, and glycerol. However, the complexity and variable composition of the aqueous phase, influenced by the feedstock and processing conditions, represent significant challenges in its valorisation. The low total organic content (typically 2-3% carbon) and the presence of many low-molecular-weight and low-value components make separation and purification of individual chemicals economically challenging.

Nevertheless, several promising approaches are being investigated to overcome these challenges. These include thermochemical conversion processes like catalytic hydrothermal gasification (CHG), biomass cultivation, anaerobic fermentation, bioelectrochemical systems, hydrothermal gasification, and recycling for HTL.

Conclusions

Comparing pyrolysis and HTL, pyrolysis opportunities primarily engages in separation technologies to parse bio-oil into valuable fractions, while HTL opportunities delves into downstream conversion to utilize the carbon content in its aqueous phase. This focus disparity makes it challenging for HTL to borrow from pyrolysis advancements due to differing bio-oil chemistries. However, pyrolysis could potentially benefit from HTL's aqueous phase solutions, as the challenges with aqueous fractions are likely parallel in both processes.

Numerous opportunities exist for creating materials and chemicals from biomass pyrolysis, particularly fast pyrolysis. Fast pyrolysis can yield substantial liquid products, also known as bio-oil, composed of various complex components. While bio-oil has established uses as an

energy carrier, exploiting its complex chemical structure could unlock more applications. Different conversion processes could transform bio-oil into a range of valuable chemicals. Fractionation methods are discussed for obtaining functional fractions from bio-oil, which can serve as precursors for green chemicals and materials. Many of these opportunities have been realized at a TRL of 6-8. Despite the promising outlook, challenges like scalability, bio-oil complexity, and product consistency need to be addressed to fully realize this sustainable and circular bio-economy pathway.

Purification of chemicals and materials from hydrothermal liquefaction (HTL) is also an area of much interest. The biocrude component, although laden with useful compounds, requires sophisticated methods for efficient separation and refinement due to its high boiling point and the wide range of polar and oxygenated compounds. The HTL aqueous phase, on the other hand, presents a rich prospect for carbon recovery and nutrient recovery for biomass production. However, its complexity, dilute nature, and the presence of low-value components constitute significant hurdles for straightforward extraction, valorization, and economic viability. Advancements in thermochemical conversion processes such as catalytic hydrothermal gasification (CHG), biomass cultivation techniques, anaerobic fermentation, bioelectrochemical systems, hydrothermal gasification, and HTL recycling might offer solutions to these issues. Nonetheless, these options are currently at a low TRL and the quest to unlock the full potential of these resources necessitates more efficient, cost-effective processes.

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