INL/JOU-21-62242-Revision-0

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October 2021

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract UI & FSU

Overview and technology opportunities for thermochemically-produced bio-blendstocks

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Abstract

Global demand for transportation fuels is projected to increase 40% by 2040, and biomass-derived fuels (biofuels) play a crucial role in substituting fossil fuels and mitigating greenhouse gas emissions. Currently, biofuels are mainly consumed as blendstocks combined with petroleum-based fuels, and effective conversion technologies can address the quality challenges for offering standalone biofuels. Thermochemical conversion process is one of the most promising pathways among existing technologies for biofuel production. However, the major barriers are unwanted characteristics (e.g., thermal instability) of intermediate products, such as bio-oil, and required upgrading treatments for producing compatible fuels. This study highlights the merits and critical challenges of thermochemical conversion and physicochemical upgrading technologies for bio-blendstock production from lignocellulosic biomass. The novelty of this study lies in potential directions for future research through both critical and systematic literature reviews, and the proposed intensified process for lignocellulosic-based fuel blendstocks production. It is concluded that recovery and fractionation strategies (e.g., quenching and stripping) can maximize process yields and add values in the efficient conversion pathways. Effective quenching can stop secondary free radical reactions and improve liquid yields over gas and solid yields. Stripping process can improve process yield, catalyst lifespan, and thermal stability. It is further concluded that physicochemical treatments are not as effective as thermochemical treatments, but have advantages of mild operating conditions and potential for integrated solutions in conjunction with other treatments.

Keywords. Lignocellulosic Biomass, Bio-oil, Biofuel, Bio-blendstock, Thermochemical Conversion, Upgrading Technology.

Abbreviations. CFP, catalytic fast pyrolysis; ESP, electrostatic precipitation; FCC, fluid catalytic cracking; FP, fast pyrolysis; FT, Fischer-Tropsch; GHG, greenhouse gas; H/C, hydrogen to carbon ratio; HDT, hydrotreatment; HTL, hydrothermal liquefaction; O/C, oxygen to carbon ratio; SP, slow pyrolysis; UC, ultrasonic cavitation.

1. Introduction

Motivation. Fossil fuels (predominantly diesel, jet fuel, and gasoline) are used extensively in different sectors (e.g., transportation, agriculture, commercial, domestic, and industrial) for various purposes, such as manufacturing operations, process heating, and electricity generation. On a global scale, the transportation sector is almost entirely dependent on petroleum-based fuels and is responsible for over 60% of the world’s crude oil consumption [1]. According to the International Energy Agency and the US Energy Information Administration, the energy produced from fossil fuels significantly contributes to greenhouse gas (GHG) emissions, which are responsible for global warming and climate change [2]. Therefore, renewable fuels (e.g., biofuels) from renewable resources (e.g., agricultural and forestry resources, algae, and municipal solid waste) are valid substitutes to petroleum-based transportation fuels key for mitigating GHG emissions.

Biofuels can address several sustainability challenges and national priorities, such as energy security, foreign exchange savings, environmental impacts, and socio-economic concerns related to rural regions. Advantageously, lignocellulosic-based biofuels significantly solve environmental issues and simultaneously circumvent ethical dilemmas between energy production and food supply chains [3]. The growing interest in widespread use and application of biofuels stems from the need to overcome two of the world’s greatest and urgent needs to (i) veer away from the unsustainable dependence on fossil fuels and (ii) mitigate humankind’s impacts on global climate change [4].

Current status. Biomass-to-biofuel supply chains suffer from the upstream (e.g., biomass supply and pretreatment) and midstream (e.g., process efficiency and product quality) challenges that increase the total production cost and reduce commercial viability [5]. In fact, the costs of current technologies for biomass pretreatment (e.g., size reduction and dewatering), conversion (e.g., pyrolysis or gasification), and upgrading make biofuel production, economically unfeasible [6]. The present operating costs of conversion and upgrading are the major cost-driver for biofuel production, consisting of over 60% of the total cost [7]. A significant research effort is being put into transforming biomass to biofuels by focusing on conversion processes, resulting in various developed technologies, including biochemical and thermochemical pathways [8]. Thus far, each technology offers unique advantages and disadvantages, however, none of them has overcome the economic barriers to become viable and sustainable.

Background. Lignocellulosic biomass (i.e., dry plant matter, consisting mainly of lignin, hemicellulose, and cellulose) has several advantages that set it apart as a convenient source for renewable energy, such as natural abundance, inedible raw materials that do not compete within the food markets, and avoidance of land-use competition [9]. The large abundance of lignocellulosic resources provides great potential for fuels and green chemicals production (Figure 1). Studies on supply chain and integrated biorefineries recommend performing pretreatments and conversion processes near collection sites, for biomass, volume, and energy densification. In this way, transporting highly compacted and high-energy density materials will reduce upstream issues and costs, instead of moving high moisture content and low-energy, large volume biomass resources.

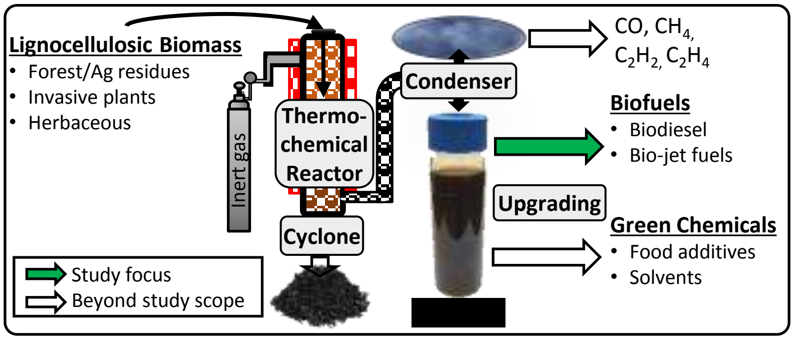

Figure 1. Biomass thermochemical conversion pathway to biofuels and green chemicals

Among the conversion technologies, thermochemical processes (e.g., gasification, hydrothermal liquefaction (HTL), and pyrolysis) have proven to be an appealing way to produce biofuel blendstocks from the valorization of intermediate products (e.g., bio-oil) [10]. A specific feedstock may be suitable for a particular process over another process, therefore, feedstock composition is essential in determining the optimal process. Additionally, pyrolysis, especially catalytic fast pyrolysis (CFP), stands out as a promising pathway for bio-oil production due to its high product quality [11]. Rapid condensation of pyrolysis vapors is essential for inhibiting undesired over-cracking. Therefore, various techniques have been considered to maximize bio-oil recovery operations, such as quenching, stripping, aerosol condensing, and fractionation [12]. These techniques attempt to avoid liquid yield losses and improve its quality by increasing the recovery rate and decreasing coking, biochar entrainment, and entrapment by the non-condensable gases.

Compared to crude oil, bio-oil exhibits a greater O/C ratio and a lower H/C ratio, determined by the presence of oxygenated organic compounds and water that, in turn, confer on a poor energy value. Productive use of bio-oil has proven challenging due to the need for enhancements before consumption. Using current combustion engines and boilers is deterred by bio-oil deficient fuel characteristics, instability, and complex chemical compounds [13]. Bio-oil can also suffer from many adverse effects regarding its quality, including incompatibility with traditional fuels due to high water and oxygen content, high solids (or ash) content, chemical instability, and high viscosity [14]. Several optional pathways (e.g., fluid catalytic cracking, hydrotreating, and electrochemical) have been considered to upgrade bio-oil to transportation fuels [15]. Upgrading objectives include (i) reducing oxygen (deoxygenation) and water content and (ii) increasing the hydrogen content (hydrogenation) to become compatible with fossil fuel components, existing combustion engines, and fuel distribution infrastructure. Figure 2 presents several key chemical reactions occurring during bio-oil upgrading processes.

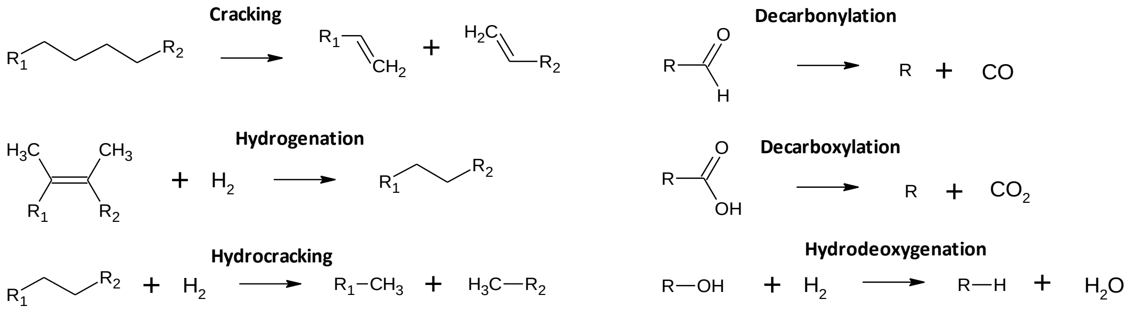

Figure 2. Chemical reactions for upgrading bio-oil to biofuels

Objective. This study applies both critical and systematic review techniques to explore thermochemical approaches and advancements of biomass conversion and bio-oil upgrading processes, as well as to identify production challenges, unsolved problems and issues, commercialization gaps, and potential solutions to address market needs. Special attention is given to the insights of current technologies to further visualize potential promises or capabilities that may address known inadequacies. Additionally, this study proposes an intensified process, including thermochemical conversion and physicochemical upgrading technologies for lignocellulosic-based fuel blendstock production.

2. Systematic Review

Systematic reviews can help in identifying and integrating previous relevant studies to ascertain the scope of existing research, and the followed trends, as well as to potentially identify gaps and contradictions, and forecast directions for future studies. The conducted search strategy herein assesses keywords, publication records, citations, and research methodologies on published studies surrounding lignocellulosic-based fuel production. Furthermore, the presented analysis covers relevant technologies related to the conversion and upgrading approaches used for functionally equivalent biofuel production. To conduct the systematic review, two databases were generated for this study, using the following keyword sets and Web of Science, searching the titles, abstracts, and keywords of published peer-reviewed articles (TS, advanced search field tag) between January 2010 and December 2020. The search results show 5,478 and 5,792 records for keyword sets 1 and 2, respectively. A comparison of the two databases found 1,064 articles in common.

- Keyword Set 1: TS = (Biomass OR Lignocellulosic) AND (Bio-oil OR Thermochemical) AND (Biofuel OR Fuel OR Upgrading)
- Keyword Set 2: TS = (Biomass OR Bio-oil OR Thermochemical OR Pyrolysis) AND (Fuel OR Biofuel OR Upgrading) AND (Electrochemical OR Hydrotreatment OR Hydrogenation OR Cracking OR Ultrasound OR Ultrasonic)

Figure 3 presents that the interest in this field is accelerating over the last ten years. From the systematic review results for the keyword searches, bio-oil production and upgrading research is rising, with the most advancement occurring over the last three years. Bio-oil recovery methods mentioned in the keyword set 1 saw increased publications in general. Keyword set 2 shows the growing interest in catalytic upgrading, electrochemical, and ultrasonic upgrading technologies reflected by the continual increase in publications during the past ten years.

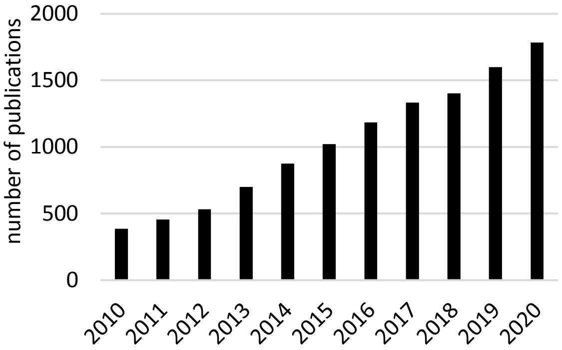

Figure 3. Increase in number of publications by year for both keyword sets during the last ten years

Figure 4 depicts subsets of the retrieved, combined publications, providing insight into subjects of interest within the keyword sets. Using keyword sets 1 and 2, the most studied technology is pyrolysis, which catalytic pyrolysis is major. During these ten years, the number of gasification and HTL publications are almost marginal. The most discussed issues were yield and quality of the products, followed by deactivation and recovery. Published studies focused more on upgrading and product slate, with much less focus on feedstock type and technology development.

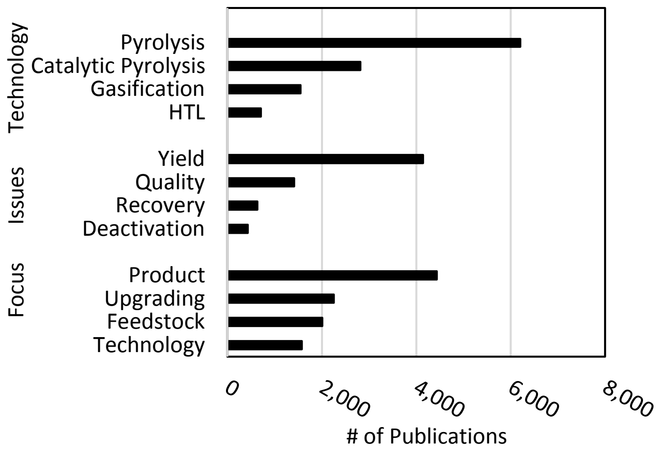

Figure 4. Classification of keyword subsets

Looking into the most cited articles of each keyword set can provide insight into popular data and topics in the current scientific community. Carpenter et al. (2014) is the most cited article in the keyword set 1 and reviews feedstock and pretreatment impact on bio-oil yield and product distribution [16]. It was found that little is known about the effects of pretreatment and feedstock, and current studies were summarized. Chen et al. (2015) appeared as the second most cited article in the same keyword search, performing a review on the thermochemical conversion (e.g., torrefaction, liquefaction, pyrolysis, and gasification) of microalgal biomass into biofuels [17]. The conversion processes and subsequent products were described. The third most cited, Lehto (2014), reviewed combustion and quality of fast pyrolysis bio-oil from lignocellulosic biomass, focusing on bio-oil burning applications [18]. They recommend that bio-oil grades should be standardized to create reliable bio-oil combustion systems, and attention should be placed on quality control from feedstock harvesting to end-use. Zhang et al. (2013) is the fourth most cited article and reviewed fast pyrolysis bio-oil upgrading techniques (e.g., hydrogenation, hydrodeoxygenation, catalytic pyrolysis, catalytic cracking, steam reforming, molecular distillation, supercritical fluids, esterification, and emulsification) [19]. Current problems and future development directions are summarized.

Gilkey et al. (2016) is the most cited article in the keyword set 2, and it presents the current progress of upgrading biomass through heterogeneous catalytic transfer hydrogenation, focusing on hydrogenation mechanisms and cleavage [20]. Challenges and future research direction to turn catalytic transfer hydrogenation into a competitive process. Luo et al. (2014) ranks as the second most cited paper, which assessed advancements for using sonication for biomass pretreatment and conversion to fuels and chemicals [21]. Ultrasound was shown to provide positive process benefits, depending on frequency and intensity. Bussemaker et al. (2013) appears as the third most cited article from keyword set 2, studying the effects of ultrasound as a pretreatment method for biorefinery applications [22]. They conclude that a mix of high-frequency ultrasound, oxidizing solutions, and the use of combined alternative augmentation techniques have the potential for reducing energy requirements and provide synergistic ultrasonic enhancement. Hu et al. (2014) is the fourth most cited article and systematically summarizes selective hydrogenation of hydroxymethylfurfural to dimethylfuran [23]. Several hydrogen donors (e.g., molecular hydrogen, formic acid, alcohols, and water) were discussed, and the reaction mechanisms of dimethylfuran, combustion performance, and safety issues of dimethylfuran.

Ultimately, the citation trend indicates a clear move towards green chemicals that represent higher value-added products compared to biofuels or bio-blendstocks, which might be an attempt to leverage the deficient economics of upgrading. Based on the systematic review results, thermochemical treatment methods (e.g., fractionation, hydrotreatment, and fluid catalytic cracking) have been extensively studied and reviewed compared to other physicochemical methods, such as ultrasonic cavitation (UC) treatment. There are 112 studies that applied UC treatment method during the past ten years, showing a growing interest and UC's potentiality. However, thermochemical methods can be considered as the leading and mature methodology compared to other methods.

3. Critical Review

A critical review was conducted to identify recent advancements and breakthroughs to elucidate the current state of biomass-to-biofuel production pathways. Particularly, the critical review focuses on bio-oil production, recovery, and upgrading to explore existing challenges and potential solutions for future research and development.

3.1. Bio-oil production

Thermochemical pathways have dominated the conversion of biomass into bioproducts (e.g., chemicals and fuels). Many of these approaches, however, utilize high temperatures and pressures and are very indiscriminate in product yield and quality, leading to the production of fuels exhibiting hydrogen deficiency and oxygen enrichment as opposed to that of conventional fossil fuels [24]. Thermochemical conversion processes (e.g., fast pyrolysis, catalytic pyrolysis, and hydrothermal liquefaction) produce varying bio-oil qualities, each with unique advantages and deficiencies.

3.1.1. **Pyrolysis**

Fast and slow pyrolysis. Pyrolysis can be categorized into two broad groups: slow pyrolysis (SP) and fast pyrolysis (FP). SP operates at moderate temperatures (300-500°C), low heating rates, and long residence times (0.2-60 min) and is more favorable for biochar production [25]. Biomass pyrolysis is the thermochemical decomposition of solid materials that can be highly affected by mass and heat transfer phenomena. Thus, parameters, such as temperature and heating rate (thermal component), as well as composition, particle size, and shape, and residence time (the chemical component), will affect thermochemical reactions and material reactivity. FP is a promising technology, using high temperatures (400-650°C), rapid heating rates (up to 1000°C/s), short residence times (below 2s), and rapid quenching of the produced vapors to achieve high liquid yield [26]. In the vein of FP, there are several different reactor designs and configurations (e.g., fluidized bed, microwave, ablative, auger, and free-fall) to convert biomass feedstocks into the liquid product (bio-oil) [27], each of these offering a range of advantages and disadvantages. Figure 5 depicts a pyrolysis scheme incorporating mixed fast and slow pyrolysis to optimize the yield and quality of products. Fan et al. (2017) reviewed the effects of process parameters, including temperature, reactor types, residence time, feed rate, and lignin characteristics, to determine the optimal parameter conditions for improving process yield and bio-oil quality [28]. However, the optimal conditions for improved yields and quality remain unknown. The understanding of the pathways and mechanisms underpins the development of more robust processes. A comprehensive review of proposed pathways and mechanisms for pyrolysis and catalytic pyrolysis of biomass components and the whole biomass was published in 2013 [29]. For hemicellulose, more recently, Zhou et al. developed a mechanistic pyrolysis model to detail its decomposition pathways during pyrolysis to improve the understanding of occurring chemistry and kinetics [30]. Suriapparao et al. (2018) analyzed the effects of biomass particle size, shape, composition, heating rate, and residence time on the kinetics of devolatilization during slow pyrolysis, and bio-oil composition in fast pyrolysis to find ideal parameters for plant scale-up [31].

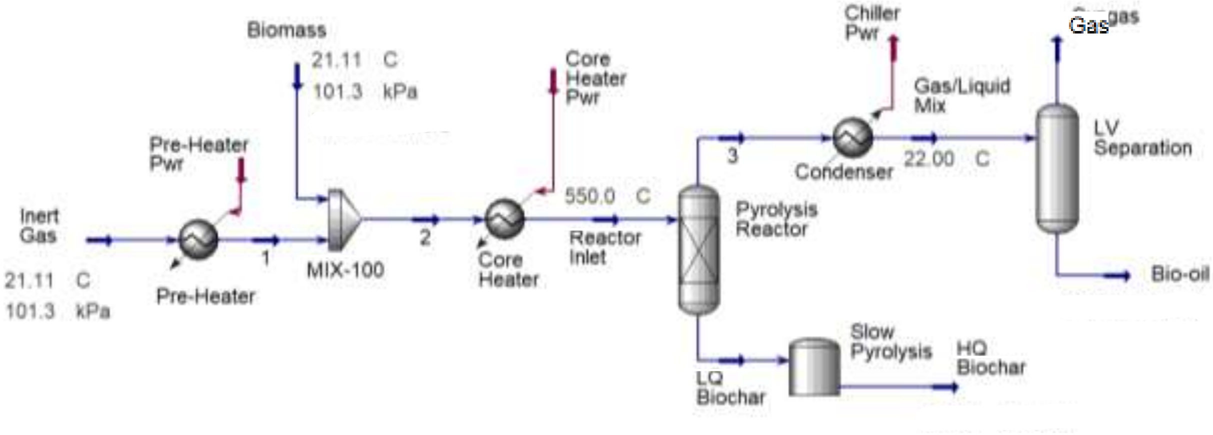

Figure 5. Aspen HYSYS scheme of mixed fast and slow pyrolysis unit [32]

Further research into pyrolysis oil characterization and analysis, upgrading methods, and reactor design optimization is required for viability. Extensive reviews of FP have been done by Bridgwater (2011), Mostafazadeh et al. (2018), and Sharifzadeh et al. (2019) [14,33,34]. As the conversion step in biofuels production, FP has not reached a commercial scale, which indicates the existence of unresolved issues and challenges. Bio-oil from FP suffers from many detrimental physical and chemical properties, including undesirable O/C and H/C ratios, high water and ash content, and low higher heating value that necessitates further chemical upgrading and prevents it from being competitive with fossil fuels [15].

Catalytic fast pyrolysis (CFP). CFP integrates catalytic transformations with FP to produce smaller molecules and improve the O/C and H/C ratios, which is more suitable for biofuels and green chemical production. CFP improves selectivity and enables the occurrence of new chemical reactions during pyrolysis (e.g., decarbonylation, decarboxylation, dehydroxylation, and hydrogen transfer), enhancing bio-oil properties through reduction of the oxygen content and of molecular weight, and changing molecular structures to be closer to that of transportation fuels [35]. Techno-economic analysis of the CFP technology estimates minimum selling fuel price as about $3.3/G for ex-situ CFP, and $2.5/G for in-situ CFP [36], positioning CFP as a viable thermochemical alternative for producing more compatible products in comparison to other conversion pathways. However, the most competitive minimum selling fuel price was assessed, using KIOR's configuration and public information, but the bankruptcy and shut down of this plant is clear evidence that economic sustainability and such competitive prices are unrealistic.

Technical feasibility and bio-oil quality improvements are supported by published data, an example is provided by Zhang et al., who performed a comparison of CFP and FP, using HZSM-5 as a catalyst and corncob as a feedstock in a fluidized bed reactor, demonstrating that the presence of catalysts reduced the oxygen content of bio-oil by 25% [37]. Ciesielski et al. reported on the role of integrated multi-scale modeling and experimentation in supporting strategies for technology development and its eventual commercialization. They emphasize the fact that isolated solutions to individual problems might not lead to holistic solutions. The improvements needed for the CFP pathway require additional clarification of physical and chemical interconnected multi-scale phenomena, as well as a multidisciplinary and multifaceted approach. The entire visualization of the challenges and their interplay for the whole process technology was suggested [38]. Catalyst screening for selective deoxygenation to improve bio-oil quality, avoiding detrimental effects on yield, was reported for many catalysts, including Al_2O_3, CaO, MgO, CuO, Fe_2O_3, NiO, ZnO, ZrO_2, TiO_2, HZSM-5, and MCM-41. The balance between yield and deoxygenation could be provided by increases in decarboxylation combined with a decrease in dehydration [39].

Notwithstanding research advancements, government funding, and predicted economic feasibility, CFP has not yet realized widespread industrial implementation [40]. One of the CFP challenges is the design of highly active, selective, and stable catalysts that could maximize the bio-oil yield of suitable quality for further processing [41]. The other and probably most relevant challenge is the development of feedstock-flexible processes, particularly processes that could cope with biomass feedstock variability [42]. Finally, process development requires an integrated view of all the unit operations involved from feeding throughout to product recovery, together with a holistic visualization for upstream (supply of conversion-ready feedstocks meeting process specifications) and downstream operations (providing a bio-oil product suitable for upgrading).

3.1.2. **Hydrothermal liquefaction (HTL)**

HTL is a thermochemical liquefaction process used to convert biomass into bio-oil at high temperature (200-400°C), pressurized conditions (3,500-6,000 psi), i.e., water sub-/super-critical conditions, which provides means for treating high moisture biomass feedstocks (e.g., algae) without the need for drying or dewatering [43]. Since pretreatment (e.g., dewatering and size reduction) of feedstock is one of the energy-intensive steps in converting biomass to value-added products (e.g., fuel, cosmetics/perfumes, food additives, nutritional supplements, detergents, and plastics), HTL can take advantage of low dewatering requirement, for reducing the pretreatment costs [44]. Additionally, catalysts are not required for the HTL process, however, there has been a significant change in gears towards using catalytic approaches to improve the quality of the products obtained by HTL technology [45].

Recent studies have investigated the effect of process conditions on bio-oil quality and yield for the HTL conversion pathway, using algae as feedstock to liquid fuels and varying temperature, residence time, and catalyst. Zou et al. achieved a maximum bio-oil yield of 26% for the HTL of microalgae *Dunaliella tertiolecta* at 360°C, and 50 min of reaction time, using 5% Na_2CO_3 as catalyst [46]. Biller et al. found that bio-oil yields were 25% higher than the lipids content of various microalgae with different biochemical compositions, using 1 M Na_2CO_3 and 1 M formic acid during HTL operation, indicating conversion products from the proteins and carbohydrates also present in the feedstocks [47]. Bio-oil yield could be increased by increasing temperature, biomass loading amount, and residence times, while water density had negligible effects [48]. Catalyst screening (Pd/C, Pt/C, Ru/C, $Ni/SiO_2{-}Al_2O_3$, $CoMo/\gamma\text{-}Al_2O_3$ (sulfided), and zeolite) under HTL processing of microalgae *Nannochloropsis* sp., and in the presence and absence of hydrogen has been reported. The only effect of hydrogen was to decrease the gas yield, and only the Ni catalyst exhibited catalytic (desulfurization) activity [49].

Although HTL initially focused on the highest moisture feedstocks, i.e., algae, it showed promising results for good quality diesel production. The net economy derived from the higher pressure (5-25 MPa) and longer residence time has hindered the commercialization of this application [43]. Further research is needed to better understand the interplay complexity of critical parameters (e.g., temperature, pressure, catalyst effect, and residence time) and broaden the application from wet biomass towards dry feedstocks. More information on HTL of biomass has been provided by Toor et al. (2011), Gollakota et al. (2018), and Ponnusamy et al. (2020) [50–52]. Nevertheless, commercialization of the HTL process technology has followed a different course of action, and currently, four companies have based their production on this technology, namely ARA ReadyFuels, Licella-Canfor, Renmatix, and Steeper Energy. This new course of action concerns the production of higher value-added products and, in few instances, is accompanied by biofuels.

3.1.3. **Gasification and Synthesis**

Gasification is another thermochemical process in which biomass reacts with a gasification agent (e.g., air, oxygen, CO_2, steam, or supercritical water) to produce synthesis gas (syngas) [53]. Operating conditions are very high temperatures (750-1,000°C or higher) and approximately atmospheric pressure. Syngas is a mixture composed of CO and H_2, with minor amounts of other compounds depending on the feedstock and process technology employed. The Fischer-Tropsch (FT) process can be used for the synthesis of hydrocarbons from syngas. In addition to hydrocarbons, methanol (and ethanol) can also be synthesized, and attractive chemicals and fuels can be derived from tandem reactions, e.g., methanol-to-olefins (MTO), methanol-to-gasoline (MTG), and ethanol-to-jet (ETJ) [54]. The produced liquid hydrocarbons from syngas are identical to those present in fossil fuels and products, requiring only mild finishing treatments [55]. Regardless of the hydrogen-depleted nature of biomass, most of the efforts have been targeting a high H_2/CO ratio of the product. For instance, Fe in Fe/CaO catalysts improved the H_2 concentration and yield for a fluidized bed gasifier [56]. Catalytic gasification has been proven a valid approach for enhancing the selectivity toward H_2 formation in the gasifier [57]. Biofuel production through the gasification pathway was only economically feasible at very high oil prices [58].

While gasification and FT synthesis are mature technologies when applied to fossil resources, but that is not the case for renewable resources. The production of hydrocarbons has also reached maturity through this pathway from carbonaceous (fossil) viscous and solid materials, such as bitumen and coal (coal to liquid, CTL processes), which biomass (biomass to liquid-type of processes) do not appear to be competitive [59]. Further information on gasification and synthesis has been provided by Molino et al. and Santos and Alencar [59,60]. At this point, it is worth mentioning that while this pathway is economically hindered for the case of biomass, it has become the preferred technology for the processing of municipal solid wastes, and several companies have centered their business model on it, such as Enerken and Red Rock.

3.2. Bio-oil Recovery

Currently, the considered conversion processes operate at a smaller scale than the processes considered for bio-oil upgrading. Therefore, bio-oil must be produced, recovered, and accumulated from a few conversion units before being fed to the upgrading unit. More than one operating unit needs to be integrated into a recovery train or system.

Some of these operating units for bio-oil recovery have been proven, and their objective is to maximize yield recovery of produced bio-oil, minimizing any organic losses through the system.

3.2.1. **Quenching**

Quenching in chemical processes refers to the rapid cooling of the reacting media to temperatures below which the undesired reactions will not occur. It is a widely practiced heat exchanging process where liquid coolant comes into direct contact with gases and vapors (Figure 6). Pyrolysis units commonly utilize quenching columns to condense pyrolysis vapors to form liquid bio-oil [14]. Standard coolants comprise immiscible hydrocarbon solvents or even recirculated liquid bio-oil. Rapid condensation of pyrolysis vapors is essential in mitigating bio-oil yield losses by preventing secondary reactions of the most reactive species (e.g., free radicals) present in the vapor phase [61]. High heat transfer rates between the vapor and coolant liquid are the main requirement when implementing quenching in pyrolysis, while one of the main advantages is the significant amounts of gas scrubbing.

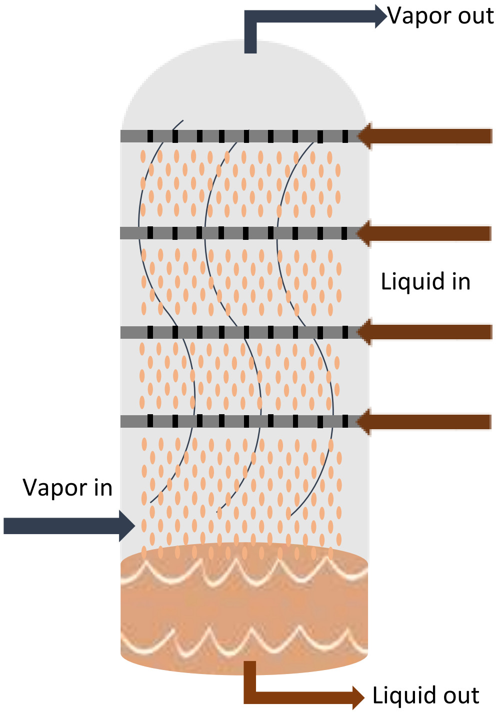

Figure 6. Quenching spray tower schematic

Spray towers/columns are commonly used for quenching. Incorporating a quenching spray tower in the FP process and using previously produced bio-oil as a quenching liquid, Shemfe et al. (2015) increased the total condensable vapor recovery factor by over 17%, with a bio-oil collection efficiency of 84%, indicating the suitability of bio-oil as quenching liquid [62]. This method was also effective at preventing tar buildup on the walls of the condenser. Using a Venturi scrubber/condenser to perform quenching with bio-oil during pyrolysis has also been shown to improve the collecting rate to 95-98% of total bio-oil produced [63]. Daugaard et al. (2015) accomplished quenching and fractionation, using various inert gases (e.g., nitrogen, helium, argon, and other noble gases) and liquids (e.g., liquid nitrogen, bio-oil aqueous phase, and other small hydrocarbons) as quenching coolants while also manipulating quenching temperature. The various recovered bio-oil fractions exhibited higher quality [64]. Isopar, an ExxonMobil refined isoparaffin product, has also been used as a quenching coolant in pyrolysis units. Isopar is lighter than bio-oil, causing isopar to accumulate at the top of storage vessels while the bio-oil sinks to the bottom, facilitating (anti)solvent recovery and recycling [65].

Regardless of the criticality of quenching in FP, publications are not as prolific as they are in other aspects of operating units of the process [66]. Quenching columns may face problems regarding flooding and heat transfer efficiency if not appropriately designed. Flooding occurs when the flow of liquid becomes restricted because of high gas velocity, which leads to the liquid getting entrained in the vapor, pulling the fluid with vapor through the column [67]. To eliminate the phenomena of flooding, a study performed by Palla et al. (2015) examined several quenching column designs to test gas flow, liquid flow distribution, and heat transfer [12]. Park et al. (2016) studied condensation characteristics by varying heat transfer conditions in quenching, such as the ratio of vapor flow rate to liquid flow rate, as well as quenching temperatures to maximize [68]. They also developed an empirical relationship for measuring the volumetric heat transfer coefficient for direct contact heat exchangers. A recent study performed by Dalluge et al. (2019) investigated the effects of cooling rates on pyrolysis vapors had on the resulting bio-oil composition [69]. A decrease in unwanted secondary decomposition reactions was noted, as well as a significant increase in bio-oil product yield. Further information on pyrolysis condensing systems has been provided by Papari et al. (2018) [70].

3.2.2. **Electrostatic Precipitation (ESP)**

ESP could be effectively used, in conjunction with quenching [71] for capturing aerosols entrained in the fluid [65]. These aerosols are fine bio-oil particles generated in condensers and exiting with the non-condensable gases [72]. Bio-oil aerosols size range from sub-micron to micron-scale [73], resulting in nearly impossible to entirely remove, using cyclones and quenching columns [74], remaining entrained in the non-condensable gas pyrolysis product. The ESP uses an electric field to generate a corona discharge, which ionizes the gas stream particles. These particles are attracted to grounded walls where they build up and are collected [75]. The liquids captured by the precipitator, along with those removed by quenching, can then either be drained to storage or recycled to the quenching unit.

Huang et al. investigated the filtration characteristics of ESP by examining several parameters, such as particle size, flow rate, voltage, and discharge polarity [76]. A train of ESPs connected in series will improve bio-oil recovery and minimize yield losses, as shown by Bedmutha et al. (2009), comparing the recovery efficiency of single and double-stage electrostatic precipitators, which were 92.4 and 93.2 wt%, respectively [77]. ESP can also be combined with condensers in the fractionation train of bio-oil. Gooty et al. (2014) used the ESP with a condenser on either side to produce bio-oil with low water content [78]. The optimized series of condensers were able to obtain an almost water-free (below 1 wt%) bio-oil in the first condenser and ESP, and a high-water content product in the third condenser. Challenges faced by ESP usage include energy conservation and ozone generation [79]. Higher collection efficiency can be achieved using a negative polarity ESP as opposed to one of positive polarity, but the increase in ozone production makes these ESP unusable indoors. Positive polarity ES, though less economical, is more widely used. More detailed information on ESP technologies and applications can be found in earlier studies by Mizuno (2000) and Jaworek et al. (2007) [80,81].

3.2.3. **Stripping**

Stripping is the physical reverse of quenching and involves using a vapor or gas stream to remove (transfer) components from a liquid stream or from a porous solid, which is generally performed in packed columns or trayed towers. The application of stripping in pyrolysis aids in increasing catalyst life span, decreasing coking, and removing bio-oil compounds entrained within the solids (e.g., heat carrier, catalyst, biochar, and ash) that leave the pyrolysis reactor [82].

Steam stripping is commonly used in petroleum refineries for catalytic cracking to reduce coking and can have a similar application for pyrolysis. Although the needs for stripping in pyrolysis are low since most heat carriers are non-porous, they can be considerably greater for catalytic pyrolysis. Thus, stripping is a common operating unit in catalytic pyrolysis [83], though a systematic study for operating conditions, design, and configurations is still pending. An earlier study on pyrolysis shows the effect of stripping on the gas product yield and the characteristics of the produced biochar [84]. The effects of stripping in catalytic pyrolysis are multiple, including product recovery, coke formation, heat balance for units with continuous regeneration, and product distribution and quality [85].

3.2.4. **Separation and Fractionation**

Fractionation is a separation process, which involves dividing and collecting bio-oils or bio-vapors under different conditions to obtain products with varying compositions. Several fractionation concepts have been proven, including distillation, extraction, and separation by solubility properties [86]. Within these concepts, several methods are practiced, focused on producing value-added chemicals and fuels while overcoming the challenges created from the complexity of bio-oil composition and properties. Pinheiro et al. (2019) extensively reviewed the methods and strategies for bio-oil fractionation [87].

Figure 8a presents the fractionation of pinewood-based oil by differential precipitation. The oil is dissolved in toluene and sequentially mixed with a solvent of increased dipolar moment (e.g., dichloromethane – DCM, methanol). The process yields two fractions: a soluble material and a precipitate. The solid precipitate is redissolved again and mixed with a solvent mixture of increased polarity. The method enables the stepwise extraction of soluble fractions with the increased dipolar moment. Molecular-level analysis, performed via atmospheric pressure photoionization coupled to FT-ICR MS, enables access to molecular properties, such as H/C (hydrogen deficiency) and O/C (polarity) ratios for tens of thousands of compounds detected for each sample. Figure 7b presents the molecular composition of pine oil and its solubility cuts, represented in van Krevelen diagrams, in which the *y*-axis represents the H/C ratios, whereas the *x*-axis features the O/C ratios. Each pixel corresponds to a unique molecular formula, and the color scale indicates the relative abundance, i.e., from gray (low) to red (high) [88]. Bio-oils are ultracomplex mixtures, which chemical separation could be challenging. Regardless of its complexity, Figure 7b indicates a slight O/C increase as a function of increasing fraction polarity. Future and ongoing efforts are focused on liquid chromatography fractionation with online FT-ICR MS detection to capture compositional trends not easily accessible by direct infusion MS [89].

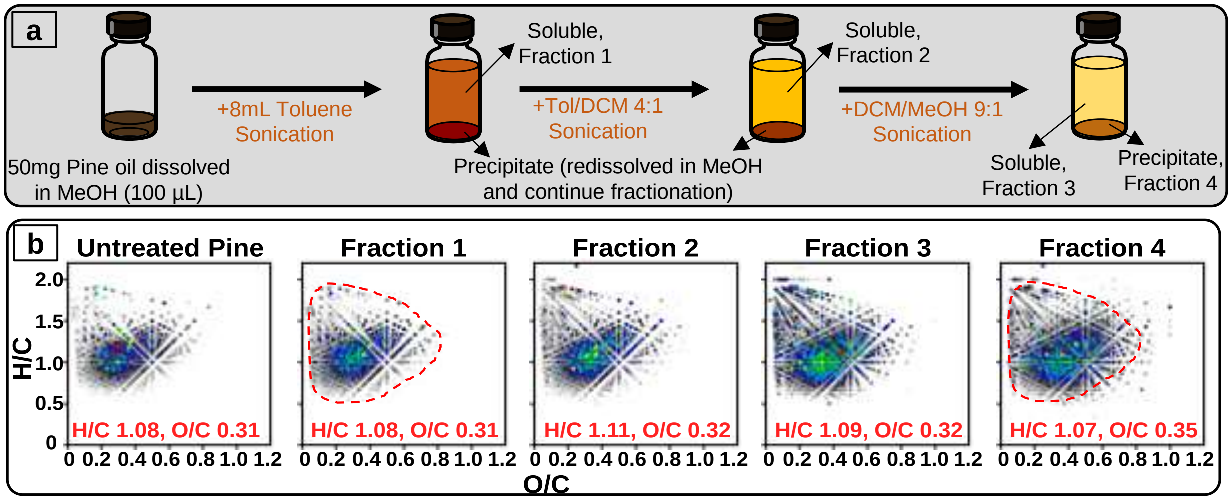

Figure 7. (a) Prior fractionation attempts on pinewood-based oil and (b) characterization results in Van Krevelen diagrams by MagLab's APPI 9.4 Tesla FT-ICR MS (H/C and O/C ratios included in Red)

Pollard et al. (2012) [90], Schulzke et al. (2016) [91], and Gooty et al. (2014) [78] conducted fractionation studies and developed bio-oil recovery systems, using stage fractions consisting of pairs of condensers and electrostatic precipitators in series, with each condenser operating at different temperatures. With this setup, water and acidic compounds were mostly condensed in the last stage, producing higher quality oil in the front stages. Persson et al. performed stepwise thermal treatment of the lignocellulosic biomass feedstocks rather than fractionating bio-oils. Biomass was first treated at 200-300°C and then 550°C, with the study revealing the pyrolytic liquid to have higher phenolics content and lower acid number than the liquid product from a single-step process [92]. The comparison of two different fractionation concepts (i) performing fractionation during liquid recovery and (ii) carrying it out after liquid recovery through phase separation resulted in oil with lower moisture content from the first concept, while the second proved to be more useful in dividing bio-oil into different compound groups [93]. While one stage condensing maximizes yield, other fractionation approaches are typically better for producing higher quality bio-oil [93]. Several fractionation approaches have been reported from different types of thermochemically produced bio-oils [94], however, there is a lack of literature focused on the optimization of fractionation conditions (i.e., number of stages, temperature gradients, and relative product composition comparisons), and also on comparison on the different fractionation approaches. Further information has been provided in published studies [87,95].

3.3. Upgrading Treatments

3.3.1. Catalytic Conversion

Two commonly used methods of deoxygenating bio-oil are catalytic cracking and hydrodeoxygenation. The specific catalytic conversion methods discussed in this article are fluid catalytic cracking and hydrotreating.

Fluid catalytic cracking (FCC). FCC is seen as a convenient way of using bio-oil for biofuels production without the need for significant capital- intensive investments, particularly for cases of co-processing with fossil feedstocks, in installed facilities (Figure 8) [96]. In FCC, bio-oil or bio-oil blend is heated to a high temperature under moderate pressure and brought into contact with a hot, powdered catalyst (acidic zeolites-based), breaking bonds of the large molecules in the absence of hydrogen. FCC is expected to show enhanced prospects for bio-oil upgrading because of its capabilities for processing heavy, complex feeds [97]. The current trend considers FCC for co-processing bio-oil with the typical petroleum feed (i.e., vacuum gas oil) in existing refinery units, resulting in a liquid hydrocarbon product that contains a small proportion of oxygenates from bio- oil [98].

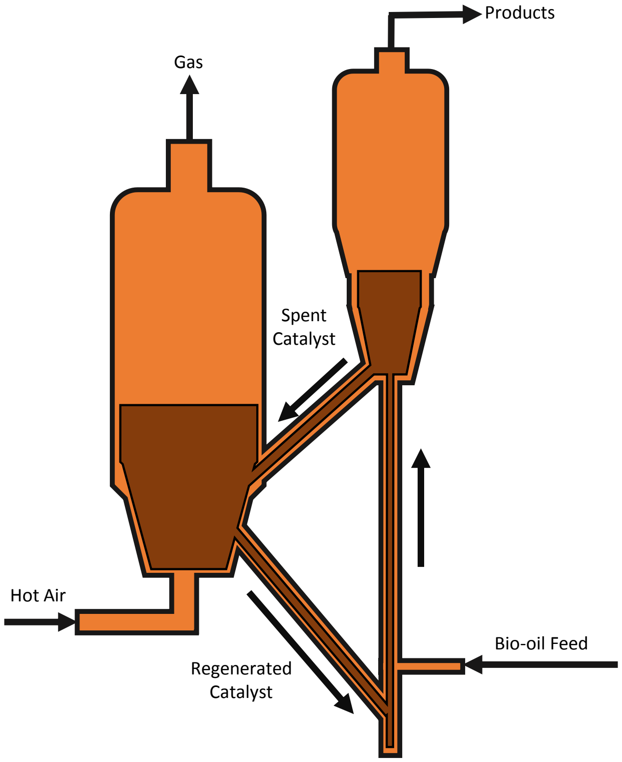

Figure 8. Schematic of a fluid catalytic cracking unit for bio-oil refining

Lappas et al. (2002) designed one of the first pilot plants for catalytic pyrolysis, producing bio-oil with reduced oxygen content and decreased molecular weight of the heavier fractions, finding significant synergies between the thermal and catalytic cracking of biomass [99]. Ma et al. (2018) used FCC to co-process bio-oil with kitchen waste oil with HZSM-5 as the catalyst, showing an improvement in bio-oil yield, inhibition of coke formation, and a significant decrease in oxygen content [100]. Studies that support the feasibility of co-processing bio-oil with vacuum gas oil are discussed and presented in a recent study [98], including some of the drawbacks of using FCC in co-processing. For instance, the buildup of coke, tar, and char leads to reactor plugging that causes major operational problems and decreases biofuel yield. These problems are greater when processing bio-oil and are diminished by co-processing with petroleum feeds due to the synergistic effect on the cracking of bio- oil, promoting the conversion of the oxygenates to liquid hydrocarbons [98]. Overall, FCC methods for treating bio-oils have proven to improve physicochemical properties. A review of FCC co-processing of bio-oil can be found in an earlier study by Stefanidis et al. (2018) [96].

Hydrotreatment (HDT). HDT of bio-oil is expected to eliminate the reactive functionalities by either deoxygenating, cracking, or hydrogenating the molecules [101]. Generally, achieving these HDT objectives requires higher pressures (above 125 bar) and temperatures (above 380 °C) compared with the conditions commonly used in crude oil refining due to the chemical nature of the oxygenated compounds present. However, in typical HDT operations, the feed is preheated to reaction temperatures, but this step is precluded for bio-oil due to its thermal instability. Hydrogenation has been suggested to stabilize the bio-oil, and noble metals have been tested for this purpose to avoid extreme heating stress of bio-oil [102]. Thus, two-step processes involving a first stabilizing step (hydrogenation), followed by hydrodeoxygenation, have been suggested and widely tested. In the first step, the most reactive functional groups, i.e., carbonyl and carboxyl functional groups, might be transformed into alcohols or decarboxylated, respectively. Formed alcohols are easier to deoxygenate and stabilize media that might allow heating at HDT required temperatures for cracking and hydrodeoxygenation [103]. Product properties, distribution, and relative yields depend on temperature, pressure, catalyst, and space velocity. HDT catalysts play a major part in determining product properties [104].

HDT reactions are advantageous when treating bio-oil. The massive presence of oxygenated compounds in pyrolysis oil has made HDT an effective processing option for the required deoxygenation when producing drop-in fuels or improving compatibility with commercial fuels [39]. Upgraded bio-oils proved to be more soluble in biodiesel, blends containing up to 38-48 wt% bio-oil, could be prepared upon HDT for augmenting solubility. HDT used a Ru/C catalyst and temperatures of 200-325°C [105]. Fundamental studies mainly focus on catalyst activity but do not address the troublesome issues found in HDT. For instance, a comparison of Ni and Ru nanospring based catalysts for the HDT of phenol (as model compound) showed better activity and conversion for Ru than Ni [106].

Catalyst deactivation in bio-oil HDT is fast enough to shorten the catalyst life cycle to hours and has precluded long-term runs, even at a pilot scale. Efforts for understanding the deactivation of HDT catalysts include both noble metal hydrogenation catalysts and common HDT formulations (e.g., CoMo and NiMo). An example is the study of sulfided Ru/C and CoMo/C using various analytical techniques, which concluded that fouling caused by condensation reactions of aldehydes and ketones and loss of the catalyst active sites by the transport of inorganic elements from the bio-oil and the reactor construction material onto the catalyst surface are causes of deactivation

[107]. Fouling consequences were confirmed by investigating temperature effects on the hydrotreatment of pyrolysis oil from mallee wood, on sulphided NiMo catalyst, at 375-450°C at 70 bar. Coke deposition was favored at higher temperatures that accelerated polymerization reactions, leading to blockage and decreased product yield [108].

The reactions responsible for catalyst deactivation, reactor plugging, and coke formation are aggravated with increasing scale due to their exothermicity [109] and are exacerbated at the industrial scale at which HDT is operated adiabatically. Bio-oil instability is probably the main responsible for these issues [87], and for this reason, one approach has been the two-step processes that includes a stabilization step [110]. In summary, the required process severity (e.g., pressure, temperatures, and heat) of existing HDT technologies, together with the operational burdens derived from the bio-oil thermal instability, have made these processes cost-intensive and precluded their commercial application. New and improved processes are needed for decreasing these high energy requirements and high operational costs, therefore, enabling the commercial production of lignocellulosic bio-blendstocks. Future work on HDT should focus on the separation of bio-oil fractions and upgrading them further to value-added products. An in-depth review of bio-oil HDT has been provided by Han et al. [111].

3.3.2. **Electrochemical upgrading**

The main use of electrochemical processes for upgrading bio-oil is electrochemical hydrogenation (Figure 9). Electrochemical upgrading of bio-oil benefits from mild operating temperatures and pressures, control over product selectivity, and water use as a source of protons for hydrogenation [112]. The electrochemical hydrogenation treatment of rice husk whole bio-oil, using platinum electrodes to investigate the evolution of aromatic structures was facilitated by producing radicals from cellulose and hemicellulose-derived species [113]. Elangovan et al. (2015) accomplished a noticeably decreased oxygen content after the electrochemical deoxygenation of pine oil in the aqueous phase in an oxygen ion conducting ceramic membrane-based cell [114]. Lister et al. (2018) designed a three-compartment electrochemical cell, for upgrading and stabilizing bio-oils prior to HDT. The upgraded pine bio-oil showed a lower total acid number, higher pH, and a reduction in carbonyl groups content, which were considered insufficient for HDT purposes [115]. Most electrochemical studies have taken an applied approach to demonstrate the feasibility of upgrading different molecules, giving a little perspective into optimized electrochemical biofuel production. To efficiently upgrade bio-oil into biofuel, it would require plotting out all possible complex compound reaction pathways involved in the conversion process [116]. A further expansion of the basic understanding of controlling selectivity throughout more competitive pathways, which might involve a contribution to deoxygenation, would be required to make this treatment option viable.

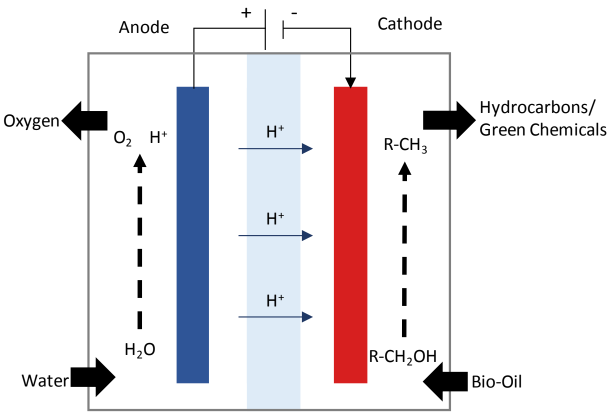

Figure 9. Electrochemical cell for bio-oil upgrading

3.3.3. **Ultrasonic Cavitation (UC)**

Though showing promise, few studies have been performed using UC to increase the quality of bio-oil. The application of UC proved to be an efficient and economically functional technique to increase biodiesel production [117]. UC facilitates mass transfer by increasing the formation of smaller particles and disaggregation of cluster and large agglomerated particles, with far superiority from other mixing methods [118]. Cavitation created by ultrasound might split heavy bio-oil molecules. The range of temperature and pressure in the cavitation bubbles might be high enough to cause the breaking of C-O bonds and the evaporation of water or emulsification with the bio-oil [119]. In this case, the treated oil would have lower oxygen content and viscosity. If the UC treatment is carried out in the presence of catalysts and hydrogen donors, the number of C-H bonds would increase, resulting in more stable oil. Once the bonds of the larger molecules are broken sufficiently, generation of free radicals will be favored, leading to reactions with other groups to form stable compounds, as shown in Equations (1)-(4) [120]:

H (1)

(2)

$$RR'CH-OOH \rightarrow RR'CHO\cdot + \cdot OH \tag{3}$$

$$RR'CHO\cdot + RH \rightarrow RR'CHOH + R\cdot \tag{4}$$

A UC-upgraded bio-oil exhibited a higher heating value, and no long-term stratification was observed upon storage for 112 days [120]. Qin et al. performed the UC-assisted upgrading of pyrolyzed pine-nut bio-oil using a methanol/n-octanol mixture as a solvent. Additionally, to the increased heating value, results also a decrease in viscosity and moisture content. It was also noted that the time and power of the ultrasonic processor had a noticeable effect on the bio-oils' physicochemical properties and stability [120]. Similar experiments using pine-nut bio-oil tested the effects of using various solvents (e.g., ethyl acetate, acetone, n-octanol, and polyethylene glycol). Out of all the solvents, n-octanol proved to be the best performing solvent, increasing heating value, and decreasing viscosity with no signs of stratification 60 days after the experiments [121]. Nevertheless, the stabilizing effect of alcohols and their energy value are well-known facts [122]. Yang and Duan used HTL bio-oil from microalgae to test the effects of frequency, power, time, and temperature to analyze viscosity and elemental composition [123]. While enhanced production of bio-oil by UC has been proved [21], UC treatments have not been directly and conclusively applied to bio-oil upgrading. All these results seem to indicate value promise from UC treatments in improving bio-oil physical and chemical properties, and subsequently, overall quality. Regardless of the promise shown, the lack of systematic and systemic studies limits a valid assessment of process efficiency or feasibility. Further details about UC treatments of vegetable oils or the upgrading of heavy oil are given in earlier studies by Kumar (2017) and Xie et al. (2015) [124,125].

4. Discussion

The current state of the transportation sector, its impact on undesirable emissions, and the imminent implementation of decarbonizing strategies bring about the use of biomass feedstocks and low-emissions energy sources in the game for more efficient production and valorization of conversion products in various forms to low-carbon and carbon-neutral fuels. The conducted critical and systematic reviews in this study offer an overview of existing lignocellulosic biomass-to-biofuel technologies, emphasizing each of the operating units that still exhibit problems and represent challenges for bringing technology to the market plate. The challenges associated with producing a stable bio-oil and the design and development of new innovative upgrading methods open the door for potential research approaches and prospects for future work. The critical review examines the leading conversion processes for bio-oil production, recovery, and valorization based on efficiency and complexity. Even with recent advancements, the development of biofuel technologies entails further investigation and advancements to overcome conversion yield inefficiencies, product compatibility, and quality inadequacies to become commercially feasible. Bio-oil primarily suffers from high water and oxygen content, high ash content, chemical instability, and high viscosity. Without integration, current pathways are insufficient, unsustainable, energy intensive, and overall ineffective.

Prior studies have conducted techno-economic assessments to identify the key parameters and cost drivers of biomass to bio-oil production pathways. Table 1 presents a comparison of these studies over the last decade. These costs only represent the costs to produce the bio-oil and do not consider further costs of upgrading. The average Brent crude oil price of 2020 was $1.43 per gallon. Even though the cost to produce bio-oil is slightly less than that to obtain crude oil, fuels produced from bio-oil are still not produced at an economically competitive price.

Table 1. Comparison of bio-oil production costs

Study	Cost ($/gal)	Feedstock	Technology	Year
Rogers and Brammer [126]	1.00	Miscanthus	Fast pyrolysis	2012
Jones and Male [127]	0.59	-	Fast pyrolysis	2012
Brown et al. [128]	1.76	Forest Residue	Fast pyrolysis	2013
Mirkouei et al. [129]	1.15	Forest residue	Fast pyrolysis	2015
Wang and Jan [130]	2.08	Rice husk	Fluidized bed fast pyrolysis	2018
Schalkwyk et al. [131]	1.09	Forest residue	Fast Catalytic pyrolysis	2020

Although some companies have currently announced their technology licensing availability, no commercial-scale bio-oil to biofuel pathway technology has been implemented. KiOR in 2013 started construction and implementation of its CFP followed by HDT pathway technology, and by the end of 2014, the production of nearly a million gallons of fuels demonstrated the technical feasibility of such technology. However, the bankruptcy filing a few months later was a clear indication of the lack of economic feasibility [132]. Therefore, further research into improving and developing various integrated technologies is deemed necessary. Several pathways for bio-oil upgrading have been reviewed by Hansen et al. [133]. So far, both CFP and HTL have been shown to be capable of producing reasonable quality bio-oils, which can be upgraded. Integration of these technologies with other hydrodeoxygenation processes could be an effective way of converting bio-oil into intermediate products compatible with existing refinery infrastructure and end-user vehicles. A fully deoxygenated bio-oil can be fractionated into drop-in biofuels or alternative hydrocarbon fuels that can meet these criteria [135]. Nevertheless, cost-effective upgrading technologies need to be developed up to a commercial scale. Clearly and regardless of the promising technical aspects of the CFP followed by HDT pathway, its economic feasibility still needs to be demonstrated. New physicochemical approaches are being studied to intensify and compliment CFP, such as electrochemical hydrogenation [115], electrocatalytic hydrogenation [136], catalytic transfer hydrogenation [137], and UC [123]. Further details about the CFP, upgrading, the advantage of multifunctional catalysts, and end products are given in earlier studies by Elliot et al. [138], Patel and Kumar [139], and Rover et al. [140].

The promise of UC could be enhanced further by integrating UC with catalytic transfer hydrogenation, leading to an increased efficiency process. Earlier studies explored the application of ultrasound in the preparation of catalysts (e.g., titanium, palladium, and Ni–Mo–B amorphous), and their effect on the performance of these various catalysts for deoxygenation hydrogenation and hydrodeoxygenation [141,142]. Preliminary results have indicated the incorporation of hydrogen from the hydrogen donor (ammonium formate) into the organic phase, however, the details of this incorporation remain unknown. Additional efforts are also needed to improve deoxygenation under the treatment conditions [143].

Aside from the need for integrated technologies, further investigation should be placed into recovery and treatment approaches that deal with the complexities of bio-oil compounds and their interactions. Understanding the physics and physicochemistry involved in the quenching and stripping processes, as well as miscibility studies, can be very useful for the design of an effective and efficient conversion pathway. Although there is no consensus on the pyrolysis reaction mechanisms, it is well accepted that it occurs via free radicals [29]. Most of the quality issues and thermal instability have their root causes in those mechanisms. Quenching is typically carried out under normal pyrolysis operations to stop free radicals' reactions. Quenching with water has been examined in the literature and practiced commercially [144]. Separating the gas, vapor, and liquid products entrained into the solid product is part of the recovery operation. If the quenching solvent is selected to dissolve all these organic entrained products, then stripping and the first stage quenching can be integrated into a single unit. However, it might be convenient to keep the product as gas and vapor and avoid condensation into liquid form for effective stripping. Figure 10 presents a schematic of a novel refinery unit that integrates discussed recovery and treatment methods. Such integrated refinery units can be beneficial for developing and modeling feasible biofuel production pathways. For the proposed multi-step pathway, each step can be studied and optimized for improving integration means and paving the way towards intensification.

Feedstock type, while not reviewed in this article, is another crucial facet to consider when optimizing product quality and yield. Particularly, lignin, hemicellulose, and cellulose are the three main components of lignocellulosic biomass, of which lignin stands out for having higher energy content. Additionally, lignin's chemical structure is suited for producing high quality chemicals and fuels with less intensive post-conversion upgrading compared to other lignocellulose components [145]. However, prior studies have reported that lignin is relatively challenging to decompose (over the range of 160-900°C) while its conversion also produces high amounts of solid byproduct [146].

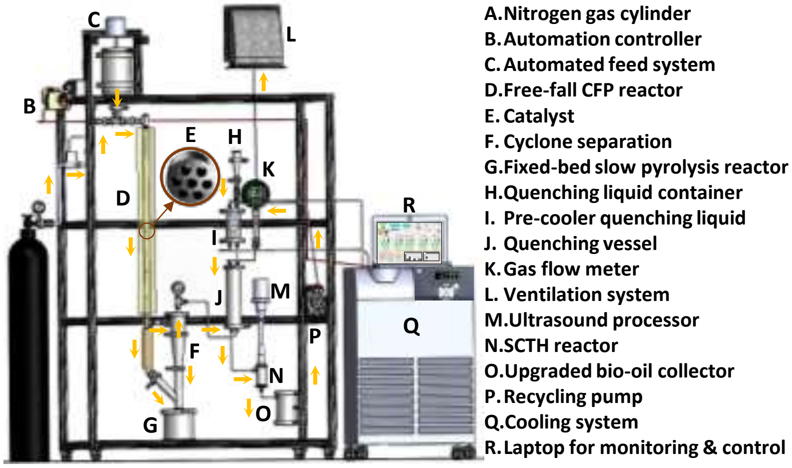

Figure 10. Proposed integrated multi-step process for lignocellulosic-based fuel blendstocks production

Prior studies have defined various chemical decomposition and fractionation techniques, which set the basis for a simple classification of isolable chemical compounds of commercial importance [147]. These techniques (e.g., high-resolution mass spectrometry and multi-dimensional hyphenated chromatographic and spectrometric techniques) are able to obtain a detailed chemical profile of compounds in each isolated chemical family. A better understanding of the composition might reveal insights into these physical, physicochemical, and chemical events. The complexity of the interplay among compounds and their root causes can interfere with catalysts, extraction, fractionation, transport, and refining or upgrading processes. The simplification attained through a multi-level chemical characterization could enable the application of advanced techniques for in-depth knowledge of obtained fractions. Particular attention should be placed on current and future generations of recovery and post-treatment technologies to enhance quality and commercial competitiveness.

5. Conclusion

This study has determined that recovery and fractionation strategies can be beneficial for maximizing pyrolysis yields and add values in the efficient conversion pathways. Effective quenching of pyrolysis vapors can stop secondary free radical reactions and improve liquid yields over gas and solid yields. Electrostatic precipitators are a simple and efficient means to recover fine bio-oil particles entrained in the gas stream. The stripping process can improve the overall pyrolysis process by decreasing coking, increasing bio-oil yield, and lengthening catalyst lifespan. Proper fractionation improves bio-oil quality, however, avoiding yield losses requires further research and optimization. The gaps in bio-oil treatment methods have been highlighted in this study. Thermochemical treatments, such as FCC and HDT, are effective, but intense process conditions are economically unsustainable. The mild operating conditions and product selectivity of the electrochemical processes are beneficial; however, the complexity of the present compounds makes it difficult to efficiently achieve desired properties in the product. The physicochemical treatments are not as effective as thermochemical treatments but have the advantages of mild operating conditions and the potential for integrated solutions in conjunction with other treatments.

Both critical and systematic reviews conducted in this study make evident that there is a need for a single-step, intensified pathway for lignocellulosic-based fuel blendstocks production. Integrated biomass-to-biofuels pathways can provide solutions to global issues (e.g., reducing GHG emissions, natural resource utilization, energy security, and economic growth in rural areas). Therefore, attention should be placed on research and development to solve the shortcomings of conventional biofuel production methods. In order to progress biomass-to-biofuel technologies and commercialization, future studies should focus on the following:

- Holistic investigation of integrated technologies (involving all steps) for commercially viable biomass-to-biofuels production pathways.
- Exploration of bio-oil recovery and separation techniques for increased quality, yield, and thermal stability, as well as innovative conversion methods, leading to less intense post-treatment processing.
- Investigation of the physics and physicochemistry involved in quenching and stripping processes, as well as miscibility studies for the design of an efficient intensified conversion pathway.
- Exploration of multi-level chemical fractionation and characterization to simplify and reveal insights into physical, physicochemical, and chemical events caused by the complexity of the interplay among compounds and their root-causes.

Acknowledgment

The authors wish to acknowledge University of Idaho for EIS Grant and Idaho National Laboratory (INL) for resources and facilities. Part of this work was performed at the National High Magnetic Field Laboratory (MagLab), supported by the National Science Foundation (NSF) Division of Chemistry (DMR-1644779), Florida State University, and the State of Florida.

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