

A comprehensive state-of-technology review for upgrading bio-oil to renewable or blended hydrocarbon fuels

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ABSTRACT

Bioenergy sources are being advanced as a meaningful environmental solution and a substitute for conventional energy sources. Bioenergy from biomass feedstocks currently comprises the largest portion of renewables in the United States. Thus, more effective process-level solutions can result in scaling-up biomass-derived energy production (e.g., biofuels). Pyrolysis, a thermochemical conversion technology, offers a commercially viable pathway to produce bio-oil from a wide range of biomass feedstocks (e.g., algae and terrestrial). Bio-oil requires further upgrading to produce final bioproducts (e.g., transportation fuels and biochemicals). This article focuses on the upgrading of bio-oil to transportation fuels (liquid hydrocarbons), highlights the critical challenges of existing upgrading technologies, and identifies the potential research directions to meet the market needs. A comprehensive overview and classification of bio-oil upgrading pathways and their competencies are presented through both comparative and systematic literature reviews. It is concluded that the biofuel production cost is highly dependent on post-conversion pathways, particularly their hydrogenation and deoxygenation capacity. Thermochemical treatments are effective, but less cost-competitive due to the intensive process requirements (e.g., heat or pressure). Biochemical treatments are inadequate as a standalone process for upgrading bio-oil. Physicochemical treatments are less effective, however, they operate under mild process conditions and could be integrated with other treatments. It is further concluded that the electrochemical approach can be effective due to the retention of hydrogen from bio-oil water content during deoxygenation.

1. Introduction

Increasing global population and standards of living, as well as local economic growth are driving the depletion of international and domestic conventional energy sources (e.g., fossil fuels) [1]. In 2018, renewable energy contribution to the total United States (U.S.) energy consumption was approximately 11% (over 11 QBTu out of 100 QBTu), and have been suggested as part of a comprehensive strategy to address national priorities, such as promoting energy security, creating domestic job, and mitigating global warming (Fig. 1) [2]. Thus, special attention should be placed on renewable energy sources (i.e., hydroelectric, biomass, geothermal, solar, and wind), particularly in the production of

fuels from biomass feedstocks, which could allow the integration of stationary energy sources with the existing transportation infrastructure [3,4].

Stationary carbon-free energy sources (e.g., solar, hydroelectric, wind, and nuclear electric power) have limited penetration into the transportation sector, which is the second largest in energy consumption (consumed 28.8% of total) after electric power sector (consumed 38% of total) in 2017 in the U.S [1]. Current established transportation infrastructures and technologies (e.g., internal combustion engines), and distribution infrastructures favor liquid fuels over other alternative solutions (e.g., electricity and hydrogen) due to numerous technical limitations (e.g., energy densities and fast charging) [5]. Biofuels from

Abbreviations: ASTM, American Society for Testing and Materials; CC, Catalytic Cracking; CFP, Catalytic fast pyrolysis; CTH, Catalytic Transfer Hydrogenation; DOE, Department of Energy; EC, Electrochemical; ECH, electrochemical hydrogenation; EPA, Environmental Protection Agency; HAME, hydroxyalkanoate methyl ester; HDO, Hydrodeoxygenation; HHV, High Heating Value; HTL, hydrothermal liquefaction; Mo, Molybdenum; NPSC, Non-thermal plasma synergistic catalysis; PHA, polyhydroxyalkanoates; SC, supply chain; SR, systematic review; UC, Ultrasonic Cavitation; U.S., United States.

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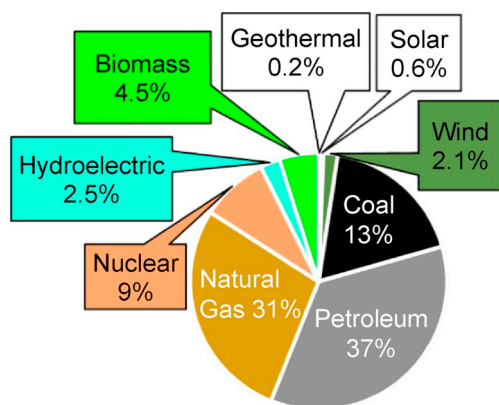


Fig. 1. U.S. total energy consumption by source in 2018.

biomass can be a promising source of transportation energy due to cheap, renewable resources, and compatibility with existing technologies, engines, and transportation infrastructure [5].

Over the past 30 years, the need has arisen for an efficient bioenergy production process to address major challenges associated with diverse biomass feedstocks, initial conversion strategies, and upgrading processes, which are responsible for high production costs [6,7]. Biomass is a promising renewable resource due to its low price and abundance [8], over 1.04 dry billion tons per year will be available by 2030 [9]. However, over 45% of biomass is underutilized due to upstream supply chain (SC) challenges (e.g., biomass collection, handling, storage, and pre-treatment processes) and midstream SC challenges (e.g., high production cost and immature conversion technologies) [8,10]. In 2017, biodiesel and other renewable fuels (excluding ethanol) were consumed at an average rate of 1.2 million barrels per day in the U.S [11]. Therefore, biofuels stand out as a key element of a comprehensive strategy to cut petroleum and coal use in half by 2030 [11]. In the U.S., distributed fuels must meet the American Society for Testing and Materials (ASTM) and the Environmental Protection Agency (EPA) standards prior to distribution. EPA has recently proposed new standards for biofuels, which are detailed in earlier studies [12,13].

The U.S. Department of Energy (DOE) and independent researchers have extensively investigated biomass conversion processes that transform biomass to energy densified intermediates, such as bio-oil, biochar, and syngas (Fig. 2) [14–16], using thermochemical conversion processes (e.g., hydrothermal liquefaction, pyrolysis, and gasification) [17–20]. Catalytic fast pyrolysis (CFP) has been suggested as one of the promising technologies among nascent thermochemical conversion pathways for bio-oil production due to high process yield and bio-oil quality [21,22]. Other CFP byproducts (e.g., biochar and syngas) have applications in food-energy-water systems as biochemicals, biochar-derived fertilizers, and wastewater filtration systems [23–25]. Recent developments from the DOE showed CFP is one of the front-runners for biofuel production. Further details about the CFP are given by Refs. [26–29].

Hydrothermal liquefaction (HTL) has been suggested for converting high moisture biomass feedstocks (e.g., algae and animal manure) to bio-oil. However, HTL requires longer residence time and higher pressure (~20 MPa) in comparison to fast pyrolysis, which increases the

operational cost and slows down its commercialization [30–33]. Recent study by Yang et al. (2016) reported bio-oil characterization from HTL of eight different algae feedstocks [34]. More detailed information on bio-oil production from HTL of algae has been provided by Guo et al. [35].

The properties and characteristics of bio-oil vary significantly between reported literature findings due to the inherent complexities of biomass' composition (e.g., furan, hydroxyaldehydes, carboxylic acids, hydroxyketones, anhydrous sugars, and phenols) and lack of control over CFP reactions (e.g., dehydration) that are not entirely understood [36–38]. Table 1 presents bio-oil physiochemical properties along with ASTM standards [13,39,40]. Besides variability, bio-oil has several associated quality issues (e.g., corrosion, viscosity, and instability), which are due to its low pH, high oxygen-to-carbon (O:C) ratio, and low hydrogen-to-carbon (H:C) ratio that indicate the quality of liquid product [36,37,41]. The high content of water and oxygenated compounds in bio-oil cause lower high heating values (HHV) of 15–20 MJ/kg compared to 45–51 MJ/kg found in transportation fuels (e.g., gasoline) [42,43]. These issues increase the amount of resources (e.g., heat and pressure) required for post-conversion treatments [44, 45].

Post-conversion treatments attempt to address bio-oil issues by producing market-responsive bioproducts (e.g., biofuels and biochemicals) [46–49]. The treatments for improving bio-oil quality and compatibility with other fuels can be divided into two categories: (a) dewatering and deoxygenation (reduces water and oxygen content) and (b) hydrogenation (increases hydrogen content) [50]. Bio-oil can potentially be used in fueling gas turbines and marine engines, however, in order to be used as biofuel in vehicle engines, it requires an energy-intensive upgrading with excessive requirements of hydrogen and catalysts [51–54].

Pre-conversion optimization of biomass treatment and supply chains have been extensively researched and are well understood [55–57], thus, this study focuses on post-conversion upgrading strategies. Based on prior techno-economic studies, bio-oil upgrading represents the largest portion of the total biofuel production cost [58,59]. Existing upgrading pathways include thermochemical, biochemical, and physicochemical processes [60]. Thermochemical upgrading processes (e.g., hydrocracking, catalytic deoxygenation, and hydro-deoxygenation) can

Table 1
Bio-oil composition matrix and associated ASTM standards [13,39,40].

Property (ASTM Standard)	Value (average)
C	56% wt.
H	6% wt.
O	38% wt.
N	0.2% wt.
S	0.02% wt.
Water content (D95, E203)	25% wt.
pH acidity (D974, D664, D3339)	2.5
Specific gravity (density compared to water)	1.2
High heating value (D240, D4809)	17 MJ/kg
Viscosity (D88, D445, D2170)	40–100 mPa
Solids (char content)	0.1%
Density (D1298, D4052)	1.2 kg/l



Fig. 2. Bioenergy products from biomass feedstocks.

alter bio-oil characteristics and composition, using heat, pressure, hydrogen, and catalysts [50,61,62]. Thermochemical processes have received the most attention due to prior use in commercialized petroleum refineries. However, direct application to bio-oil has been impeded by the intrinsic chemical differences between petrochemical and biomass precursors [63]; as well as other thermochemical process challenges, such as high energy usage and hazardous conditions [64,65]. Table 2 summarizes the recent review studies published in Renewable and Sustainable Energy Reviews on techno-economic and environmental assessments of bio-oil production and upgrading, using thermochemical conversion processes.

Chemical and biochemical upgrading pathways (e.g., esterification, transesterification, and acid hydrolysis) can alter intermediate products (e.g., low-grade fuels) properties, using chemical solvents or biological treatments without added heat [79–81]. Integrated physicochemical upgrading processes (e.g., electrochemical and ultrasonic cavitation) use electricity as the primary energy source to improve bio-oil quality, using cavitation, electro-deoxygenation, and blending that involve both

physical treatments and chemical reactions [82–84]. In other words, electricity can be applied directly or converted to mechanical waves that initiate other chemical reactions [85].

In this study, a literature review, focusing on bio-oil upgrading technologies, is conducted using systematic and comparative techniques to (a) identify the chronological evolution of reported studies, (b) explore the existing challenges, solutions, and advancements, and (c) define research and development gaps on bio-oil upgrading and biofuels production. Upgrading methods are discussed to provide an overview of the current state of existing technologies to identify high potential processes that can address persistent deficiencies and enhance aspects of sustainability in conjunction with smart manufacturing breakthroughs. Additionally, unsustainable or suboptimal strategies and methods are reviewed to gain a better understanding of requirements, intricacies, and opportunities for the future growth of biomass-derived fuels industry.

2. Systematic review

Scholars have limited time to maintain an up-to-date knowledge of the state-of-the-science and recent breakthroughs. Literature reviews, therefore, play an essential role to help the investigators identifying the key variables and bridging the research gaps. The conducted systematic review (SR) study herein covers relevant bio-oil upgrading technologies for biofuel and blended fuels production, which are currently being developed as potential conversion pathways to meet market needs. SR aims to reduce bias from the author as opposed to comparative reviews that often reinforce partialities and author's research interest. SR aids in identifying the major parameters of previous works to guide future studies by exploring the state-of-the-art in existing and next-generation conversion technologies. Two databases are generated in the Web of Science, using the following keyword sets, and a total of 273 papers are reviewed as part of the systematic literature review. It is apparent from SR that interest in biofuel production from bio-oil is increasing, as shown by increasing publications for each keyword set in the last ten years, from January 2009 to December 2018.

- Keyword Set 1: (Bio-oil OR Biofuel) AND (Thermochemical OR Pyrolysis) AND (Hydrogenation OR Ultrasound OR Ultrasonic OR Esterification OR Electrochemical) AND (Renewable OR Sustainable OR Sustainability)
- Keyword Set 2: (Biomass OR Feedstock) AND (Bio-oil OR Pyrolysis-oil OR Pyrolysis) AND (Hydrocarbon OR Transportation OR Bio-fuel) AND (Hydrogenation OR Synthesis) AND (Renewable OR Sustainable)

The primary factors influencing the increased interest in bio-chemicals and biofuels from biomass are recourse scarcity and greenhouse gas emission reduction [86]. Fig. 3 presents a comparison of the number of publications during the last ten years, using both keyword searches. A consistent increase in publications is an indicator of growing interest in biofuel production from bio-oil with the exception of 2018, showing a slight decrease in keyword set 1. Also, 2009 was the only year both keyword sets yielded an identical number of results.

Gallezot (2012) is the first most-cited article in keyword set 1 that provides an overview of valuable chemicals produced from biomass, but did not focus on bio-oil produced from pyrolysis, which has been shown to be most viable conversion pathway [86]. Wang et al. (2013) also appeared in both keyword sets, and is the second most-cited in keyword set 1 [87]. They provided a review study on hydrotreatment of bio-oil, including an in-depth discussion of bio-oil composition, and function of noble metal catalysts (e.g., Ru, Pd, and Pt). They also reported that noble metal catalysts provided the best conversion rates with less deactivation issues [87]. Rhodium was shown to be the most effective catalyst, while Molybdenum (Mo) catalyst was shown to be unstable due to sulfide formation. They focused on CFP bio-oil and substituted

Table 2

Economic and environmental review studies for bio-oil production and upgrading.

Study	Overview	Year
Hossain and Davies [66]	A review study on pyrolysis liquids and gases from biomass feedstocks was conducted to explore the potential as renewable fuels for internal combustion engines.	2013
Cambero and Sowlati [67]	A review study on economic, environmental, and social aspects of biomass to renewable products was provided to assess the potential impacts on job creation, emission mitigation, and capital growth.	2014
No [68]	A review study was provided on bio-oil applications to transportation fuels, heat, and power generation from lignocellulosic biomass.	2014
Sharifzadeh et al. [69]	This study explored economic and environmental aspects of biodiesel production from microalgae, using pyrolysis conversion technology.	2015
Raheem et al. [70]	This study discussed the thermochemical conversion technologies (e.g., pyrolysis, gasification, and liquefaction) for biofuels production from microalgae.	2015
Shen et al. [71]	This study overviewed fast pyrolysis of lignocellulosic biomass feedstocks to value-added products.	2015
Patel et al. [72]	A review study on thermochemical conversion technologies was provided to explore techno-economic and life cycle assessment for bioenergy production from lignocellulosic biomass.	2016
Mirkouei et al. [30]	A techno-economic and optimization review study was conducted for upstream and midstream segments of biomass to bio-oil supply chains.	2017
Roy and Dias [73]	An overview of economic and environmental aspects of pyrolysis technology was provided for renewable energy production.	2017
Pires [74]	This study reviewed the most recent advances in algae-based bioproducts for CO ₂ capturing and biofuel production to meet the United Nations agreement and mitigate GHG emissions.	2017
Kumar et al. [75]	A review study on three thermochemical technologies (i.e., hydrothermal liquefaction, gasification, and carbonization) was conducted for bioproduct production from biomass feedstocks.	2018
Skaggs et al. [76]	Detailed analysis of biofuel production from organic wastes was provided on a site-specific basis, using hydrothermal liquefaction.	2018
Dai et al. [77]	A review study on the technological and economic challenges of integrated torrefaction with pyrolysis was presented for lignocellulosic biomass feedstocks.	2019
Ahmad et al. [78]	A review study was conducted for bioproducts from oil palm biomass. They expected oil palm biomass can improve the sustainability and commercialization of biomass-derived renewable energy.	2019

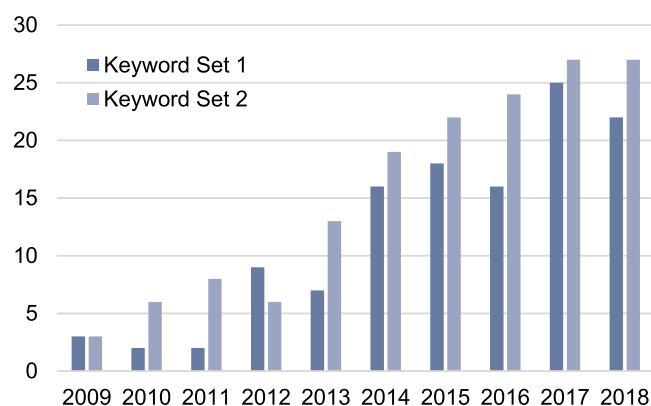


Fig. 3. Comparison of published articles for both keyword sets during the last 10 years.

compounds. In addition to the top two most-cited articles in keyword set 1, Venderbosch et al. (2010) ranked as the third most-cited article and presented stabilization of biomass-derived pyrolysis oils and the issue of rapid polymerization of bio-oil, which inhibits dehydration of the oil [88]. They suggested that bio-oil can be mildly hydrogenated immediately after biomass conversion, in order to reduce overall issues and energy use associated with upgrading later [88]. Demirbas et al. (2011) appeared as the fourth most-cited article and performed a general overview of conversion technologies, pyrolysis-based oil treatments, and various biofuel types. They concluded that many of conversion technologies lack compatibility with transportation fuels (e.g., diesel and gasoline) [89]. They also reviewed biological pathways (e.g., anaerobic digestion), but they did not cover post-conversion and upgrading process mechanics, which are the primary challenges to commercialization [89].

In keyword set 2, Gallezot (2012) and Alonso et al. (2010) are the most-cited articles [86,90]. Alonso et al. provided an overview of biomass feedstock types and its subsequent conversion technologies to intermediate bio-oil or ethanol products, however, this study lacks review of post-conversion processes and upgrading technologies to drop-in biofuels [90]. Zhou et al. (2012) ranked as the third most-cited article and studied chemical and fuels production from lignocellulosic biomass [91]. They also reviewed thermochemical pathways, focusing mainly on biomass pre-conversion technologies, as well as integrated hydro-processing for producing fuels. They identified CFP as a front-runner for commercialization of sustainable biofuels, but did not extensively discuss upgrading pathways [91]. Donnis et al. (2009) appeared as the fourth most-cited article [92]. They studied rapeseed oil and fatty acid methyl ester as two biological-based feedstocks. They extensively covered hydrogenation, chemical reactions, and effects of various hydrotreatments that may be applicable in some ways to CFP bio-oil. However, these treatments are primarily for diesel production as opposed to gasoline, and many differences exist between CFP-based bio-oil and rapeseed oil or fatty acid methyl ester, primarily CFP bio-oil is incompatible with many catalysts due to coking [92].

All most-cited articles in both keyword sets were published before 2013; since then, bio-oil upgrading technologies have advanced significantly. Thus, an up-to-date review study is necessary. Keyword set 1 had fewer citations than keyword set 2 since it included fewer thermochemical processes. Table 3 presents the top five productive organizations with the highest level of authorship in each keyword set. National Natural Science Foundation of China has the most publications of any organization in both keyword sets.

Table 4 reports the top ten countries with the most publication records for both keyword sets. The top three countries are identical for both keyword sets (i.e., USA, China, and Malaysia), most likely due to abundant biomass resources. Malaysia, for example, is a top producer of

Table 3

Top five productive organizations based on the number of publications.

Keyword Set 1		Keyword Set 2	
National Natural Science Foundation of China	14	National Natural Science Foundation of China	22
U.S. Department of Energy	8	Chinese Scholarship Council	5
Chinese Scholarship Council	4	Fundamental Research Funds for Central Universities	5
Canada Natural Sciences and Engineering Research	4	U.S. Department of Agriculture	3
Fundamental Research Funds for the Central Universities	3	National Key Basic Program of China	3

Table 4

Comparison of top ten countries with the most publication records for both keyword sets.

Keyword Set 1			Keyword Set 2		
Countries	Publications	Percent	Countries	Publications	Percent
USA	39	32.5	USA	57	35.0
China	30	25.0	China	40	24.5
Malaysia	7	5.8	Malaysia	12	7.4
Canada	6	5.0	India	10	6.1
England	6	5.0	Canada	8	4.9
Japan	6	5.0	Denmark	7	4.3
Brazil	4	3.3	Germany	6	3.7
India	4	3.3	Italy	6	3.7
Italy	4	3.3	Netherlands	5	3.1
Netherlands	4	3.3	Japan	5	2.1

Palm Oil [93]. Chinese interest in biofuel from lignocellulose biomass has been driven in part by recent food shortages and population growth [94]. After the U.S., China, and Malaysia with a total of 96, 70, and 19 publications, respectively, eight of the top ten countries are identical in each keyword search.

3. Comparative review

3.1. Thermochemical processes

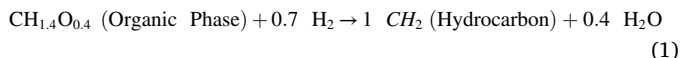
The most common upgrading technologies utilize heat and pressure to initiate chemical reactions and address bio-oil deficiencies (e.g., energy density and corrosiveness), as well as separate bio-oil into distinctive fractions that can be altered via catalytic treatments and hydrotreating [95,96]. Existing petroleum refinery technologies that utilize high temperature and pressure have shown potential for upgrading bio-oil and other biomass-based intermediate products using various upgrading practices (e.g., hydroprocessing and fluid catalytic cracking) [49,97]. Although the thermochemical upgrading technologies for bio-oil are similar to petroleum refinery approaches, bio-oil is incompatible with existing infrastructure and requires stabilization due to its high water and oxygen content [46,98].

3.1.1. Catalytic cracking (CC) and hydrocracking

CC process produces biofuel via the breakdown of bio-oil into low-carbon aromatics and light olefins; alkylation of aromatics with olefins produced C8–C15 hydrocarbons similar to diesel [99–101]. Upgraded bio-oils using CC have met some ASTM requirements based on the combustion heat, viscosity, and freeze point, which represents a promising substitute for the use in conventional petroleum refineries [102, 103]. Gollakota et al. (2016) provided the most extensive review of thermochemical technologies and reported that the average CC temperature was 478 °C [60]. Jurulluh et al. (2015) reported that CC operated at temperatures of 750–850 °C, which shows different process configuration strategies between studies [104]. Corma et al. (2007) used CC to reduce bio-oil oxygen levels, using zeolite catalyst [105]. Zeolite remains as one of the most highly effective catalysts for CC treatment, as

reported in recent studies [99,106].

Hydrocracking (a variant of CC) uses supplemental H_2 in addition to high temperature ($400\text{ }^{\circ}\text{C}+$) and catalyst to break longer molecular chains (e.g., carbon-carbon bonds) and achieve conversion yields of up to 20% for gasoline fractions [107]. Bio-oil compounds react with hydrogen through a catalyst at high temperatures to reduce oxygen and water content [108]. During hydrocracking, bio-oil vapor reacts with H_2 molecules to create alkanes (a molecular chain that comprises high-grade hydrocarbon fuels), such as cyclohexane. Hydrocracking approach for bio-oil upgrading is effective, but less cost-competitive due to the intensive process requirements (e.g., heat and hydrogen pressures) [109–111]. Equations (1) and (2) below show hydrocracking, where R_1 and R_2 are arbitrary hydrogen-carbon groups constituting a larger bio-oil molecule [112].



3.1.2. Hydrotreatment

Hydrotreatment (e.g., hydro-deoxygenation, hydrogenation, and hydro-desulfurization) refers to conventional processes, used in today's petroleum refineries, operating at high-temperature ($310\text{--}375\text{ }^{\circ}\text{C}$) in conjunction with supplemental H_2 and catalyst to remove oxygen and sulfur in the form of H_2O and hydrogen sulfide (H_2S), a highly toxic chemical [111,113,114]. Hydrotreating is primarily driven by the breaking of carbon-nitrogen, carbon-oxygen, and carbon-sulfur bonds in reaction with H_2 [112] to produce benzene and cyclohexane, and increasing the H:C ratio (Eqs. 3 and 4) [41,115,116]. In a similar way that steam reforming allows for hydrogen production from hydrogen-rich gas (e.g., natural gas, methane, and syngas); hydrogen could be produced during thermochemical processing of biomass feedstocks. Further details can be found in earlier studies by Refs. [117–119].



Hydrodeoxygenation (HDO) refers to oxygen removal from oxygen-containing compounds as opposed to H_2 supplementation [60]. Gollakota et al. (2016) reviewed 60 HDO studies for various temperatures and pressures, the average temperature and pressure of HDO was $364\text{ }^{\circ}\text{C}$ and 4.42 Mpa (641 psi), respectively [60]. Several metal-based catalysts (e.g., Ruthenium) have been tested for improving HDO, however, high catalysts cost and reusability are persistent issues [46,50,111]. Han et al. (2016) reported that Ruthenium showed resistance to deactivation in the presence of water, an issue that typically plagues other catalysts [50]. Limiting factors for HDO catalysts are low-cost, reusability, coking resistance, and effectiveness [120]. Catalyst life cycle is currently limited to less than 200 h as a result of coking [41]. Table 5 shows the bio-oil components before and after HDO. Alkanes (e.g., propane, butane, and methane) are products of hydrocracked bio-oil [41,44].

Traditional hydrocracking and HDO of crude oil results in the formation of hydrogen sulfide, which poses a significant health hazard and is extremely corrosive [112,121,122]. Earlier studies reported that one of the benefits of producing biofuels from bio-oil is its low sulfur content (approximately 0.02% wt.) [107,123]. Table 6 compares two effective thermochemical treatments based on temperature and pressure range, as well as chemicals and catalysts used in prior studies [43,60,112,124].

3.2. Physicochemical treatments

Physicochemical treatments lack the effects of externally applied heat, chemicals, or catalysts. Rather, physical treatments benefit from lower hazards, fewer consumable inputs, and generally enhanced

Table 5

Bio-oil components before and after treatment.

Component	Untreated (%)	Treated (%)		Bio-oil component range (%)	
		HDO	Hydrocracked		
Guaiacols	34.2	10.3	0.0	Acids	13–16
Acids/Esters	19.8	25.2	0.0	Esters	2–5
Ketones/Aldehydes	13.8	25.1	0.0	Phenols	10–18
Furans	11.7	6.8	0.0	Aldehydes	3–9
Phenols	10.3	18.6	0.0	Ketones	8–10
Other	6.8	3.4	5.6	Ethanone	1–2
Alcohols	3.5	5.3	0.0	2-Hydroxy	3–4
Aromatics	0.0	0.9	11.5		
Alkanes	0.0	4.5	82.9		

Table 6

Hydrotreatment comparison.

Treatment	Temperature ($^{\circ}\text{C}$)	Pressure (Mpa)	Chemical and Catalyst
Hydrocracking	500–700 (avg. 478)	0.67–0.70 (avg. 0.00)	H_2/CO ; CoMo, HDS, NiMo, and HZSM-5.
Hydrodeoxygenation	300–600 (avg. 364)	<20 (avg. 4.42)	Ni–Mo and Co–Mo supported on Al_2O_3 ; Fe/ SiO_2 (iron-based catalyst).

sustainability. As emerging technologies, they have not proven as effective as thermochemical or biochemical treatments, however, they could be incorporated as integrated solutions if used in conjunction with other treatments. Physicochemical treatments include electrochemical, plasma, ultrasonic cavitation, and mechanical blending, as described below.

3.2.1. Electrochemical (EC)

EC stabilization and upgrading of bio-oil does not require external hydrogen and can be performed at a wider range of temperatures and pressures [11]. As a byproduct, EC upgrading produces H_2 that can be used as a final product or an in-situ supplement for downstream HDO processes [11,125]. EC uses electricity to generate hydrogen protons (H^+) on the anode side of an electrochemical cell (Eq. (5)). H^+ is then transferred to the cathode side through a cation exchange membrane, where the hydrogenation of the organic bio-oil molecules proceeds (Fig. 4) [11,82]. Equations (5) and (6) show chemical reactions occurring at the anode and cathode site, respectively. The net reaction (Eq. (7) combines Eqs. (5) and (6)), such as anode and cathode reactions to explain the full EC process [82]. Equations (8)–(10) use representative

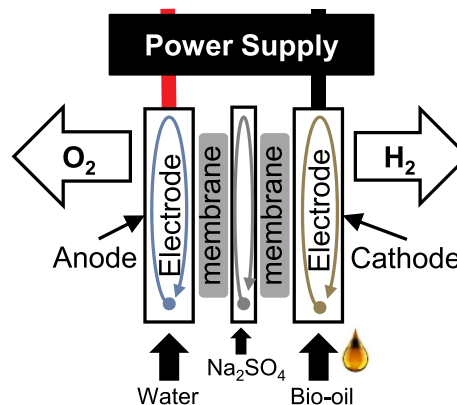
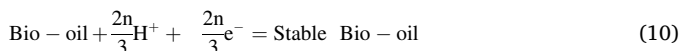
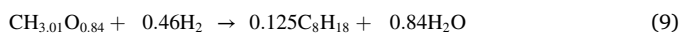
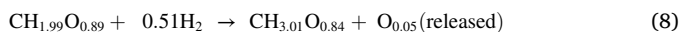
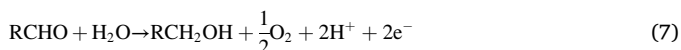


Fig. 4. Electrochemical setup for bio-oil upgrading, dual membrane systems have been used to remove bio-oil carboxylic acids.

C, H, and O composition of bio-oil to show the electrochemical hydrogenation (ECH) process impacts on H:C and O:C ratios as reported by Lam et al. (2017) [11]. Equations are based on molar composition, where n denotes an arbitrary numerical value.



ECH effectiveness depends both on the exact bio-oil composition and the surrounding chemical environment, e.g., conductivity and acidity [83]. Earlier studies reported that hydrogenation of unsaturated C–C bonds is more effective than the hydrogenation of C–O bonds [126–128]. Benzoic acid is one example of a carboxylic group found in bio-oil that can be reduced to alcohol when aided via ECH [129]. Li et al. (2012 and 2014) investigated EHC for upgrading surrogate compounds (e.g., water-soluble fractions of bio-oil and phenolic compounds), using Ruthenium catalyst [83,130]. The high viscosity and low conductivity of bio-oil require the use of membrane electrode assemblies [131]. The ionic membrane acts as the conducting electrolyte for proton transfer. Poor conductivity of bio-oil requires the use of membranes to increase effectiveness, but requires further research prior to actual use, since raw bio-oil has not been tested [11,63,82].

3.2.2. Plasma

Non-thermal plasma synergistic catalysis (NPSC) process uses the application of an electric field within bio-oil to ionize or energize electrons and radicals [132]. NPSC approach reduces energy requirements (the need of external heat) and environmental emissions [133]. Catalysts (e.g., HZSM-5 and Pt-Re/Al₂O₃) can improve NPSC, and has been demonstrated as a potential conversion pathway with several benefits, such as in-situ hydrogenation and 47% deoxygenation when tested on surrogate 4-methylanisole (i.e., a synthetic bio-oil compound) [132–135]. However, upgraded NPSC products are still considered hydrogen deficient, and catalyst suffered from extensive coking (i.e., deactivation) [133]. Maximum calculated conversion yield and deoxygenation rates were approximately 46% and 19%, respectively [132]. Pulsed NPSC was also used by Mosallanejad et al. (2017) to examine the effects on deoxygenation, and conversion rates of coronal discharge [132]. The highest deoxygenation was observed at 5 kHz and 32 W, while greater conversion to phenols occurred at 20 kHz and 54 W power. Adjusting pulse frequency impacted distinct bio-oil compounds and electrodes spacing on the test apparatus impacted conversion yield by 10% [132].

Earlier studies explored the effect of different parameters (e.g., gas type, temperature, and emission), using the plasma process to upgrade bio-oil [136–138]. Hosseinzadeh et al. (2015) investigated the effect of gas type, voltage and pulse repetition frequency on non-catalytic upgrading of 4-methylanisole as a lignin-derived bio-oil, using dielectric barrier discharge plasma reactor [139]. They concluded that (1) temperature, electron energy, and density are the major factors, (2) transalkylation, demethylation, and hydrogenolysis are the key reactions, and (3) 2,4-dimethylphenol, 4-Methylphenol, and p-xylene are major products, and (4) the highest conversion reached to 29% at the discharge power of 77 W when the argon is used as a carrier gas [139]. Guenadou et al. (2012) developed a thermal plasma apparatus for converting bio-oil to hydrogen and carbon monoxide [140]. They

investigated the effect of high temperature on the process yield of hydrogen and the formation of particles and tar [140].

Recent studies compared the effect of non-catalytic dielectric barrier discharge plasma and catalytic plasma treatments, using various catalysts (e.g., Ni, Co–Mo, Ni–Mo, Pt–Re and Pt–Cl supported on Al₂O₃, as well as HZSM-5) on hydrodeoxygenation reaction and bio-oil upgrading [141,142]. Zhao et al. (2018) concluded that the quality of upgraded bio-oil, using non-thermal plasma assisted HZSM-5 was improved and the amount of catalyst deposit reduced by around 4% [142]. Taghvaei and Rahimpour (2019) resulted that hydrodeoxygenation challenges can be addressed via catalytic plasma reactor, and the highest conversion and deoxygenation reached to 92% and 65%, respectively in the presence of Pt–Cl/Al₂O₃ and Pt–Re/Al₂O₃ catalysts [141]. The most common plasma reactor configuration consists of quartz tubes, which act as a dielectric insulator between two concentric electrodes (Fig. 5) [132,139,141]. Bio-oil is then fed dispersed in a gas carrier, while high voltages (>10 kV) are applied with different current frequencies.

3.2.3. Ultrasonic cavitation (UC)

Ultrasound generator uses a transducer, amplifier, and probe to convert approximately 60 Hz into high-frequency mechanical energy (~20 kHz) [143]. Ultrasound equipment is user-friendly and operates under mild conditions, such as low pressure and temperature [144]. Various frequencies may be utilized for different purposes, e.g., high frequency causes cavitation and blending while the low frequency can encourage compound separation [145,146]. High-frequency waves from ultrasound generate micro-scale rise and the collapse of air cavities (e.g., cavitation) within the bio-oil [147]. Energy release from each micro-implosion is minimal, although cumulative effects can be significant [147,148]. Additional effects of UC are thermal scission, free-radical generation, and sonoluminescence, which indicate molecular alterations and other associated phenomena [148,149]. Fig. 6 shows heavy bio-oil fraction and the cavitation that causes temperatures and pressure to reach 5000 °C and 10 Mpa, respectively, via ultrasound treatment [150].

Ultrasound-induced cavitation has previously seen extensive use in food processing facilities for its use in reducing long molecular chains; similarly, cavitation of bio-oil “cracks” viscous oxygenated molecules, thus reducing bio-oil corrosion, viscosity, and instability reduction [151, 152]. Splitting molecules allows to address bio-oil deficiencies (e.g., high oxygen, water content, and viscosity) through the destruction of C–O bonds and the formation of C–H bonds, using various catalysts and hydrogen donors [147]. UC treatment can also aid in the fractionation of bio-oil, as well as chemical conversion of muskmelon and vegetable oil

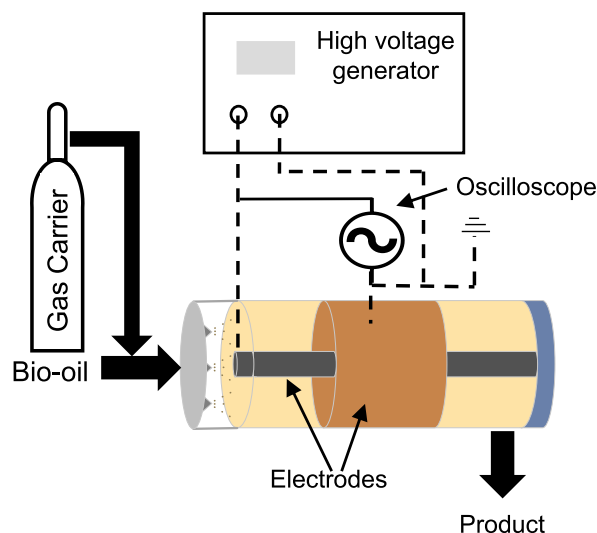


Fig. 5. A schematic of plasma setup for bio-oil upgrading.

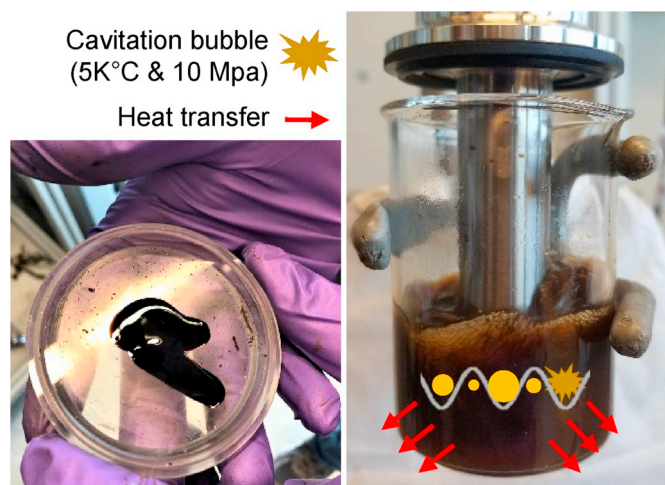


Fig. 6. Heavy bio-oil (left) and ultrasound cavitation for bio-oil upgrading (right).

to biodiesel [145,153].

3.2.4. Mechanical blending

As an alternative to addressing bio-oil deficiencies, untreated bio-oil may be blended with other hydrocarbons (e.g., diesel and gasoline) or alcohols (e.g., ethanol and methanol) in small fractions [154–156]. It should be noted that traditional practices (e.g., mechanically blended biofuels) can result in diminished performance, such as fuel separation and oxidation. Other issues, for instance, the acidity and corrosiveness of bio-oil resulted in damage to fuel delivery components of a diesel engine during extended testing [157]. However, microscopic fuel blends (e.g., emulsion fuels) can increase blended fuel stability if surfactants (e.g., chemical modifiers) are used during blending to mitigate long-term stability issues and enable usage in existing equipment [158–161].

High-frequency ultrasound (e.g., 20 kHz) can increase biofuel emulsion stability [162]. Examples of bio-oil being used in a biodiesel blend showed that many of bio-oil issues (e.g., acidity, flash point, viscosity, emissions, and low HHV) could be addressed, using bio-oil emulsions [146,163]. The greatest advantage of blended biofuel is the reduction in emissions and reduced or eliminated upgrading requirements [102]. Details regarding the combustion of hydrocarbons and their respective emissions can be found in the earlier studies by Refs. [164,165]. Xiu et al. (2012) discussed thermochemical, chemical, and blending as the primary bio-oil upgrading strategies. The production cost is the major limiting factor for bio-oil upgrading, biochemical extraction and HTL (similar to CFP with increased pressure) have been suggested as alternative steps for producing higher quality bio-oil [43].

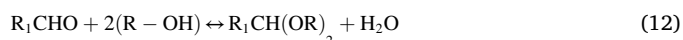
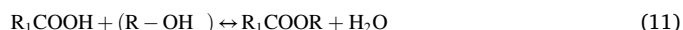
3.3. Biochemical

Chemical and biological processes (e.g., transesterification and esterification) benefit from low capital cost, small-scale suitability, low hazard, and mild operating conditions due to low temperature and pressure in comparison to thermochemical approaches [48,81].

3.3.1. Esterification

Esterification uses alcohol-based solvents for the conversion of carboxylic acids to esters. Addition of alcohols to aldehydes, ketones, and sugars produce acetals [81,166]. Catalytic esterification (using Co–Zn/HZSM-5 catalyst) reduces acid values, water content, and viscosity at a greater rate than without catalyst [119]. Schulzke et al. (2017) esterified bio-oil using butanol, zinc oxide, and zeolites, which reduced H₂O content and viscosity at 90% and 70%, respectively, and increased HHV from 16 to 31 MJ/kg, approximately 48% [167]. They

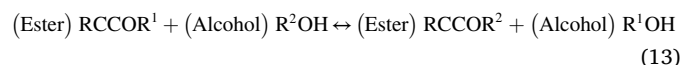
reported that the upgraded bio-oil is compatible with gas turbines and boiler fuels (e.g., heating oil or diesel #1), which have applications in heat and power co-generation plants [167]. Ciddor et al. (2015) provided an extensive review of the esterification process mechanics and chemistry [166]. Equations (11) and (12) show non-catalytic esterification reaction to form esters from carboxylic acids and the formation of acetals from aldehydes. $R-OH$ and $2(R-OH)$ represent alcohols used in each equation, where R notation indicates a generic carbon-hydrogen group [166].



3.3.2. Transesterification

Transesterification utilizes alcohol to substitute long chains in esters with smaller carbon chains, which separates residual H₂O content, reduces viscosity, and increases pH [167,168]. However, the high solvent (e.g., ethanol or methanol) ratio to bio-oil raises sustainability concerns due to water contamination [166,169]. Biodiesel produced from transesterification requires lower upgrading operations in comparison to transportation gasoline, which is highly dependent on the type of biomass feedstocks used in the pre-conversion segment [79,81]. Additionally, biodiesel produced via transesterification exhibited higher combustion efficiency and cetane value, as well as lower sulfur content, biodegradability, toxicity, and particulate emissions compared to petroleum-based diesel [170].

Zhang et al. (2017) reported on high-temperature transesterification (200 °C) with low molecular mass alcohols (such as methanol, 1-propanol, ethanol, 2-propanol, and 1-octanol) for 6–50 h duration to examine impacts of heat treatment in conjunction with transesterification [171]. For instance, they reported that 1-octanol reduced viscosity by 17%, however, it was less effective for stabilization [171]. Equation (13) outlines transesterification, where esters (acidic compounds present in bio-oil) are converted into hydrogen-rich alkyl groups (an intermediate biofuel component) and R^n notation indicates a generic carbon-hydrogen group [101,168]. The primary difference between transesterification and esterification is that esterification produces an ester and H₂O as final products, whereas transesterification uses an ester as a reactant, and produced alcohol and modified ester as final products.



3.3.3. Catalytic transfer hydrogenation (CTH)

CTH uses H₂-rich donors in the presence of catalysts to add hydrogen to bio-oil compounds (Table 7) [172–175]. Bio-oil hydrogenation via CTH approach at mild temperature and pressure reduces hazards associated with using pure hydrogen. CTH with physicochemical treatments (e.g., ultrasonic cavitation) can effectively increase the chemical reaction rate and improve bio-oil quality and H:C ratio (Fig. 7) [176,177].

3.3.4. Biological

Biochemical conversion pathways (e.g., enzymatic and acid hydrolysis) are designed for conversion of a limited, specific range of biomass to maximize productivity [178,179], which are not suitable for

Table 7

Catalyst and hydrogen donor candidates for CTH.

Catalyst	Hydrogen Donor
Ni–Cu (Nickel and copper)	NH ₃ (Ammonia)
Pd (Palladium)	NH ₄ HCO ₂ (Ammonium formate)
Pd/C (Palladium on carbon)	HCOONa (Sodium formate)
Ru (Ruthenium)	HCO ₂ K (Potassium formate)
Carbon Nanotubes	Furfuryl Alcohol

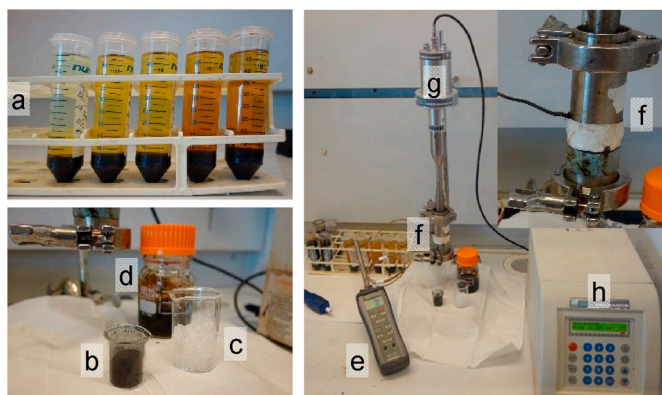


Fig. 7. Bio-oil upgrading, using CTH with UC, (a) emulsion fuels, (b) Pd/C catalyst, (c) NH_4HCO_2 (Ammonium formate), (d) untreated bio-oil, (e) digital thermometer, (f) high-pressure/-temperature CTH vessel, (g) ultrasound transducer, amplifier, and probe, and (h) ultrasound processor.

distributed (portable) production due to high capital cost and biomass specificities [178,180]. Although developing processes (e.g., microbial electrolysis) can be used in place of energy-intensive hydro-treatments to produce H_2 from aqueous bio-oil fractions for upgrading as a sustainable H_2 source [181,182]. Aqueous fractions of pyrolysis-based oil were treated, using a bacterial strain (*Pseudomonas putida* KT2440) that converts Phenols, Guaiacols, Furfural, and other substrates into useable chemicals and decreases post-treatment requirements [98]. Microbial polyhydroxyalkanoates (PHA) produced via bacteria growth in bio-oil can be used to create polyesters and have been investigated for use in chemicals and biofuel production [183]. 3-Hydroxybutyrate methyl ester and hydroxyalkanoate methyl ester (HAME) are two biofuel additives resulting from PHA, which have been tested as a substitute for ethanol. The estimated cost for biofuel from HAME was \$1200/ton; the U.S. gasoline was roughly \$700/ton in 2017 [2,184,185]. Biological processes for upgrading bio-oil have been limited largely due to bio-oil toxicity, which is detrimental to bacteria growth [98]. Consequently, alternative biological pathways are being investigated for suitability for integrated energy systems [186]. Brown et al. (2007) investigated an integrated thermochemical and biological pathway that fermented bio-oil, however, the upgrading costs were not competitive with conventional upgrading practices [187].

4. Discussion

As of yet, a cost-competitive conversion pathway for biofuels production from pyrolysis-based oil has not been achieved; thus, the opportunity remains for investigating either new or integrated technologies to improve existing approaches. During the past two decades, several technologies and conversion pathways have been presented and integrated (e.g., biological, chemical, electrochemical, and ultrasonic) to maximizing efficiency and profitability of individual entities to maintain competitiveness in the market-place. For example, current biochemical technologies can improve some aspects of bio-oil, such as viscosity and acidity, but they are incapable of fully upgrading bio-oil to transportation fuels because they are not able to reduce oxygen content (wt.%) and increase hydrogen content and heating value, which are major biofuel quality parameters.

Integrating various energy systems is one of the promising strategies to address upgrading costs for producing biomass-based transportation fuels and other byproducts, using new inventions and growing initiatives (e.g., low-pressure CFP, flow-through UC, and advanced high-temperature electrolysis [188–190]), as well as low emission energy from micro-scale reactors [191]. An integrated conversion process can not only reduce capital costs and requirements but also simplify the process as a whole to reduce operational costs [192]. Determination of

the most efficient conversion pathway is difficult, however, Xia et al. (2016) showed an increase in conversion efficiency (28% wt.) via integrated HDO with catalysts (e.g., Pt/NbOPO₄) [193]. However, Won et al. (2017) performed an analysis between multi-step and single-step processes, showing single-step conversion resulted in less energy use and lower operating costs compared to multi-step strategies [192].

Biofuels sourced from bio-oil can be market competitive if upgraded towards a single valuable liquid hydrocarbon blendstock, such as bio-jet fuel [45,194]. According to the U.S. DOE, jet fuel represents approximately 12% of total transportation fuels in the U.S [195]. Previous work focused on bio-jet fuels, however, elucidation of the complex compounds and commercial viability issues has not been addressed [196–199].

There are several similarities and differences (e.g., temperature and pressure ranges) between upgrading pathways (e.g., hydrocracking, HDO, and hydro-desulfurization) for producing petroleum-based fuels and biomass-based fuels. Thermochemical temperature ranges vary between prior conducted studies, therefore, differentiating the various thermochemical treatments can be difficult. Gollakota et al. (2016) provided a detailed outline of previous researchers who used catalytic cracking, though many listed temperatures well below the accepted threshold (e.g., 350 °C) to be considered as a thermochemical operation [60]. Fischer Tropsch synthesis was excluded from this study because it is intended for upgrading the primary product of gasification conversion process (i.e., syngas) rather than the primary product of pyrolysis process, which is bio-oil [200].

Bio-oil produced from CFP in comparison to crude oil must be amended prior to integration with existing petroleum refineries or distribution as a hydrocarbon substitute [42,112,192,201]. Meanwhile, existing biofuel production practices cannot meet the energy market needs, however, supplementing biomass with hydrogen-rich fossil fuels (via co-firing waste oil or coal) during the initial thermochemical conversion of biomass-based oil can be an approach to address the stated bio-oil deficiencies and biofuel commercialization challenges [202–204]. Graca et al. (2013) demonstrated that co-processing of hydrotreated bio-oil with crude oil (with ratios up to 20% and 80%) could produce gasoline fractions essentially identical to pure crude oil-based fuels although catalysts and hydrogen consumption remained an important issue. Similarly, non-renewable hydrogen-rich fuel sources that are, otherwise, considered as wastes (e.g., plastic, tires, and scum) can boost hydrogen content of untreated bio-oil and address other issues when co-processed with biomass [99]. Also, hydrogen can be produced from bio-oil for in-situ hydrogenation, however, the existing conversion technologies are immature and inefficient [53,117]. Regardless of the treatment and profitability challenges, biofuels generally have fewer NO_x and SO₂ emissions and consequently emit less CO₂ eq. and particulate matter (e.g., PM_{2.5}, PM₁₀) when compared to petroleum-based fuels [43,205–208].

Recent studies also investigated various conversion pathways to convert algae feedstocks (e.g., *Nannochloropsis Oscillatoria*, and *Chlorella Vulgaris*) to high-quality bio-oil, using HTL process along with catalysts (e.g., Pd/C, Pt/C, Ru/C, Rh/C, Pd/HZSM-5, and nickel) and hydrotreatment to improve the bio-oil quality and yield [209–211]. Rathack et al. (2019) studies bio-oil production via HTL of algae and bio-oil upgrading by catalytic hydrotreatment under around 360–400 °C and residence time around 2.5–10 h [212]. Liu et al. (2018) reported that the catalytic HTL process, using Rh/C catalyst achieved the highest bio-oil yield (over 50%) with HHV of 30 MJ/kg [213]. Galadima and Muraza (2018) explored the role of heterogeneous catalysts (e.g., metals, zeolites, and silica-alumina) during HTL of algae and bio-oil upgrading into hydrocarbon fuels [214]. Yang et al. (2017) investigated bio-oil properties and components from HTL of algae and liquid acid catalysts (i.e., acetic acid and sulfuric acid) [215]. Their results indicated that bio-oil H:C ratios and HHV increased in the presence of liquid acid catalysts, however, the addition of acid catalysts did not improve the bio-oil yield from HTL of algae [215]. Xu et al., [2018]

provided a literature review on catalytic HTL of algae and the catalytic effects on bio-oil upgrading [216].

Fig. 8 presents how bio-oil compares with petroleum distillate compounds, which can be separated, using fractional distillation [217, 218]. The fuel distillation curve is an important parameter that can be advantageous for understanding the complex transportation fuel properties and performance. Low distillation temperature indicates the respective molecular size, volatility, viscosity, and combustion temperature of each fraction [51,206]. Traditional processes fractionally distill crude oil into suitable products (e.g., diesel, jet fuel, and gasoline) before treatment [219]. However, as opposed to attempting the conversion of the whole fraction, bio-oil upgrading processes to high-grade fuels via physical and chemical treatments (e.g., HDO, UC, and ECH with catalysts, hydrogen donors, and solvents) can gradually reduce contaminants, O:C ratio, and low-quality components, as well as consequently increase the H:C ratio.

Biochemical pathways (e.g., esterification and transesterification) are enticing due to low capital and operational costs and mild operating conditions. However, the disadvantages of biochemical upgrading approaches are high solvent and catalyst consumption. Chemical treatments are best suited for biodiesel production as opposed to gasoline as a result of less stringent diesel ASTM standards. Esterification and transesterification as batch processes are difficult to upscale. Esterification and transesterification are inadequate as a standalone process for upgrading bio-oil due to high bio-oil oxygen content, which requires higher deoxygenation than chemical upgrading processes have achieved.

UC can impact bio-oil through co-treatment with transesterification and phase separation via hydrolysis, which can separate oil and water fractions. UC treatment can also act as a blending tool for the emulsion of residual water content or combining bio-oil with diesel fuel for the use in combustion engines. UC is advantageous due to mild operating conditions and its lack of toxic chemicals [150]. UC is able to reduce bio-oil viscosity and water content independently and proves effective as a supplementary treatment with other upgrading technologies, such as transesterification. However, tolerances between studies vary due to differences in resources used, equipment, process parameters, and bio-oil composition. In comparison with HDO, UC has not been extensively investigated or proven, however, UC can improve the process efficiency and reaction time of catalyst intensive chemical treatment. Commercial scale UC facilities will require further testing to elucidate the effects of reaction parameters and high capital cost.

EC treatments are currently under development for improving bio-oil quality and addressing other upgrading challenges. Plasma approaches used relatively higher voltage (25 V+) than EC (0.1–10 V), but energy analyses for each technology would need to be performed separately to determine the process efficiency and profitability. For example, the primary issue regarding the EC technology is membrane fouling and instability to bio-oil, and the low bio-oil conductivity that limits the effectiveness of the reaction [220]. The unique benefit of EC treatment is the retention of hydrogen from H₂O content during deoxygenation, which reduces supplemental hydrogen needed for future upgrading. EC conversion pathways are similar to other non-thermal technologies since operating conditions are mild. Though proven to affect bio-oil quality, EC cannot be considered effective yet since it is not capable of producing useable liquid hydrocarbons. However, EC applications to stabilize the

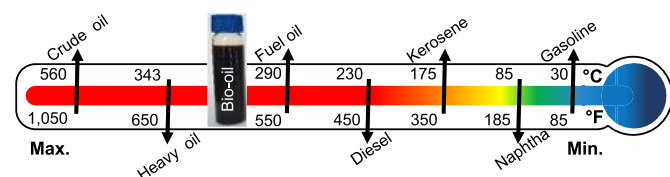


Fig. 8. Distillation scale of bio-oil and other liquid hydrocarbon mixtures [217,218].

bio-oil by reducing the acid content have been performed by Ref. [82]. Although, bio-oil to biofuel conversion processes with EC approaches have not been demonstrated as viable pathways due to existing intricacies, there is a significant opportunity to advance these approaches from their current state.

Based on the number of published articles from the conducted SR between January 2009 and December 2018 (Fig. 9), thermochemical technologies have been developed and utilized extensively in comparison to other technologies and published studies combined. The number of studies, using biochemical, physicochemical, and thermochemical technologies have been 315, 48, and 1,889, respectively. There are only nine studies of EC technology during the past ten years. Thus, thermochemical technologies can be regarded as the prominent methodology for investigation since this sector was the primary topic of 84% of all publications, discussing bio-oil treatment strategies. Moreover, esterification has received more attention than transesterification based on the results (number of published articles) of conducted SR in this study. Also, the biological methods have received the least amount of investigation due to several issues and could benefit the most from further investigation. Therefore, particular attention should be placed on current and future generation of post-conversion technologies to enhance commercial competitiveness and techno-economic sustainability benefits across the renewable and blended hydrocarbon fuels industry.

5. Conclusions and future directions

Over the past decade, the need has arisen for more innovative, efficient upgrading and valorizing carbon-based materials in various forms to cost-competitive products, using biomass feedstocks and low-emissions energy sources. The comparative and systematic reviews presented herein provide an overview of existing bio-oil-to-biofuel technologies, process and product challenges, potential science and engineering research paths, and opportunities for future work. The comparative review investigates the prominent conversion processes for bio-oil upgrading based on complexity, efficiency, and profitability. Despite recent improvements, bio-oil upgrading technologies will require further investigation and advancements to overcome process deficiencies (e.g., yields) and product shortcomings (e.g., quality and compatibility) to become commercially viable. The primary bio-oil quality issues are low hydrogen content and high oxygenate content, which impact most other attributes. Existing upgrading approaches are either energy intensive, unsustainable, or ineffective as standalone processes.

This study has determined that upgrading strategies are best indicated by their hydrogenation and deoxygenation capacity, as well as process requirements (e.g., heat and pressure). Thermochemical treatments (e.g., hydrocracking and HDO) for bio-oil upgrading are effective,

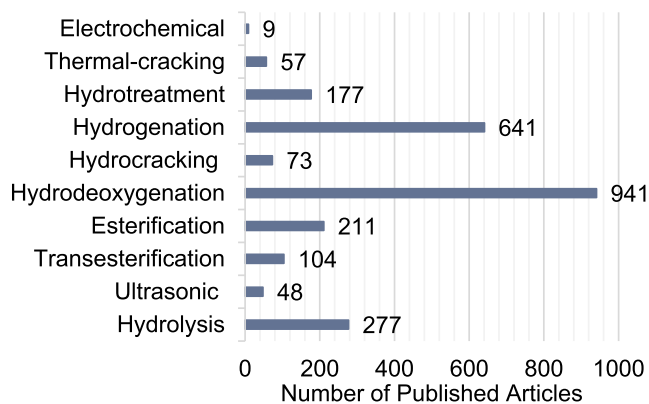


Fig. 9. Number of published studies for each bio-oil upgrading technology between January 2009 and December 2018.

but less cost-competitive due to the intensive process requirements (e.g., high temperature or pressure). Physicochemical treatments (e.g., UC and plasma) are not as effective as thermochemical or biochemical treatments, but they have mild operating conditions and could be incorporated as integrated solutions in conjunction with other treatments. UC can improve the process efficiency and reaction time of catalyst intensive chemical treatment. Esterification and transesterification are inadequate as a standalone process for upgrading bio-oil. EC approach can be considered effective due to the retention of hydrogen from bio-oil water content during deoxygenation, which eliminates supplemental hydrogen required for producing useable liquid hydrocarbon blendstocks.

This study highlights the gaps and bio-oil upgrading strategies, which are dependent on the end product specification and designation, such as mid-range bio-oil products for co-processing or drop-in biofuels. Biofuels have been most extensively tested for blended fuels production, as this approach represents the most economically favorable pathway to commercialization. This path still requires remedial bio-oil treatment prior to blending. Co-processing of bio-oil with petroleum as a secondary step utilizes thermochemical upgrading techniques, which are energy intensive and unsustainable. On the other hand, widespread implementation of biofuel blending with petroleum-based fuels may improve emerging technology success in industrial applications. Underdeveloped technologies (e.g., UC, HTC, and EC) can be promising alternatives, which need further investigation. Additionally, optimization of current technologies, using real-time monitoring and characterization can help achieve cost competitiveness and sustainability of each respective technology.

From both comparative and systematic reviews, it is clear that there is an essential need to continue development of biomass-to-biofuel conversion pathways as this represents a major viable solution to various national priorities: energy security, use of diverse domestic natural resources, advanced bio-industries and rural economies, and the dramatic environmental consequences attributed to the use of fossil fuels (e.g., greenhouse gas emissions). Thus, significant research and developments are needed to overcome the drawbacks of traditional bio-oil upgrading and biofuels production practices. Further research to advance bio-oil upgrading technologies and commercialization of biomass-based transportation fuels are as follows:

- Exploration of integrated energy systems (e.g., catalytic pyrolysis, micro-scale nuclear reactors, high-temperature steam electrolysis) for biofuels production from biomass feedstocks and low-emission energy resources (e.g., nuclear steam and heat).
- Development of blended fuels production from blending bio-oil with renewable and petroleum-based fuels, using quenching and emulsification, along with UC to bring the biofuel industry closer to economical mass production.
- Exploration of tightly coupled existing mild treatments (e.g., ECH, CTH, and UC) with commercialized thermochemical practices, using modeling and simulation approaches for input-output analysis to investigate the total resources used (e.g., energy and catalysts) and fuel produced.
- Development of a real-time chemical and spectral characterization of bio-oil and biofuel products to optimize the conversion processes, using cyber-physical advances for diagnostic and prognostic assessments to understand various intricacies of each operation.

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Appendix A. Supplementary Data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rser.2019.109548>.

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