Advanced separation strategies for up-gradation of bio-oil into value-added chemicals: A comprehensive review

Kanchan Drugkar [a], Wadilal Rathod [a], Tanima Sharma [a], Abhishek Sharma [a,*], Jyeshtharaj Joshi [b,c], Vishnu K. Pareek [d], Lalita Ledwani [e], Urmila Diwekar [f,g]

[a] Department of Chemical Engineering, Manipal University Jaipur, Rajasthan 303007, India
[b] Department of Chemical Engineering, Institute of Chemical Technology Mumbai, Maharashtra 400019 India
[c] Marathi Vidnyan Parishad, Mumbai, Maharashtra 400022 India
[d] Department of Chemical Engineering, Curtin University, Kent Street, Bentley, Perth, WA 6102, Australia
[e] Department of Chemistry, Manipal University Jaipur, Rajasthan 303007, India
[f] Vishwamitra Research Institute, 368 56-th Street, Clarendon Hills, IL 60514, United States
[g] Departments of Bio, Chemical, and Industrial Engineering and the Institute for Environmental Science and Policy, University of Illinois, 1200 W Harrison St, Chicago, IL 60607, United States

ARTICLE INFO

ABSTRACT

This work gives an outline of current research patterns in bio-oil separation techniques and their applications. Due to unpredictable nature of bio-oil, various challenges have been reported in downstream operations. Several methods have been presented to redesign the bio-oil by separating the combination of bio-oil compounds into a group of chemical substances and portions advanced in definite groups of chemical mixtures. In this review, different separation strategies for bio-oil such as fractionation, water extraction, organic solvent extraction, supercritical fluid extraction, and membrane separation, with the qualities of bio-oil extracts and their applications have been discussed. It was found that the most favorable techniques are fractionation and organic solvent extraction. The present review focuses on recent developments made from model mixtures present in bio-oil as well as pyrolysis bio-oil; techno-economical analysis has been presented for researchers who are expected to bridge knowledge gap and for industrial practitioners.

1. Introduction

Petroleum-based resources are central to the economies of all the developed and developing nations throughout the planet. The consumption of non-environmental friendly energy sources with adverse effects of their use on the environment, like global warming, have encouraged a significant interest in developing technologies that are sustainable and green. Sustainable energy sources, for example, solar, wind, geothermal, hydropower, etc. have hence acquired a ton of consideration in recent times. They have a potential to provide practicable solution to the increasing energy crisis as well as to the environmental concerns. Lignocellulosic biomass (LCB) or simply biomass also acts as a renewable and sustainable resource for the creation of various forms of energies and other value added chemicals.

Biomass is typically characterized as a material in any type of natural matter or waste from vegetation like wood buildup, agrarian waste/

deposits, creature compost, metropolitan solid(food) squander furthermore, a wide extent of various materials (homegrown waste and land clearing tasks inferred squander) [1]. Cellulose (40–50%), hemicellulose (20–40%), and lignin (20–30%) are the major constitutes of lignocellulosic (LCB) along with minor constituents like ash, protein, silica, and waxes [2]. In northern India, burning of agricultural residue (stubble) is a significant area of concern as it is a major contributor to air pollution. Thus, the conversion of these agricultural residues and other waste biomass to useful fuels and chemicals is of great importance [3]. This conversion of biomass to useful products is carried out by various thermochemical processes including gasification, pyrolysis, hydrothermal liquefaction, torrefaction, carbonization, etc. [4,5]. The major products of these processes are biogas, bio-oil, and biochar; the product distribution relies upon the sort of interaction used. The liquid product i. e., bio-oil is majorly produced via pyrolysis and liquefaction [6,7].

Bio-oil is a free-flowing, dim brown, natural fluid which is a

perplexing combination mainly comprising oxygenated compounds of around 400 varieties with different functional groups. Bio-oils are additionally alluded to as pyrolysis oils, pyrolysis fluids, bio-raw petroleum, and pyroligneous acids [8,9,10]. Chemically bio-oil contains compounds like water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids, hydroxyaldehydes, hydroxyketones, sugars, and phenolics [9]. These mixtures can be partitioned into a few families, including light fluid solvent oxygenates, furanics, phenolics, sugars, anhydrosugars, and large oligomers [3,11]. Numerous phenolic oligomers have likewise been recognized representing near 30 wt% of the bio-oil [4]. Many of these species are reactive and add to surprising characteristics. Bio-oil can be said to be a microemulsion where consistent stage is fluid arrangement of holocellulose decay items and other phase contains particles from lignin decay [12]. There are different variables that impact the immediate use of bio-oil like the heterogeneous composition of bio-oil and the instabiliy of bio-oil due to oxygenated compounds [13,14]. Also, the high water and oxygen content makes bio-oil unsuitable for the use as a fuel directly [5,15]. Thus, further treatment and processing of bio-oil is required. There are several bio-oil upgrading techniques reported in the published literature to improve its fuel properties; these include catalytic cracking, deoxygenation, steam reforming, hydrotreating, esterification, emulsification, etc. [14,4,16].

As discussed in the preceding text, bio-oil contains various chemicals and chemical groups. The separation of bio-oil to attain these valuable chemicals can be of great advantage economically. Bio-oil can offer major advantages over biomass due to the ease of handling and storage; at the same time it is a vital source for wide range of organic compounds and specialty chemicals. The objective for separation of bio-oil relies on separating various organic compounds of interest such as phenolics, aromatics, acids, and sugar derivatives by the various available techniques. Recently, researchers are studying the use of separation technologies like liquid–liquid extraction [17], distillation [15], fractional condensation [18], adsorption [19], crystallization [20], etc. to extract specific chemicals or separate certain chemical groups from bio-oil. This review discusses these separation technologies from a chemistry and process point of view. Several alternative flowsheets have been proposed, together with their economic analysis and potential applications of the extracted chemicals. Each fraction separated from bio-oil has economical value. Phenol which is a major product from the bio-oil has various advantages. It is utilized as disinfectant in household cleaners and in mouth washes. It is also used as a starting material to make plastics and find wide applications in dye industries. Other phenols such as the cresols are utilized majorly as wood preservatives. Other derivatives of phenol such as the vanillin and eugenol are used in fragrance industry. These are distinctly detected in bio-oils post separation. There are other value added chemicals extracted from bio-oil such as the furan methanol which in mainly utilized as a monomer for furan resins. These are some of the key objectives behind the bio-oil upgradation using separation technologies.

Pyrolysis is a thermochemical operation in which biomass converts into the bio-oil, gases, and bio-char [7]. The variation in pyrolysis process can result into differences in bio-oils; they can have high viscosity, corrosiveness and thermal instability. Parameters that effect the type of bio-oil are type of feedstock, size distribution, water content, reaction temperature and heating rate. These parameters significantly influence the bio-oil yield and properties. As per published data, bio-oil may contain about 70 wt% of dry biomass, which offers promising liquid feedstock for fuel and bio-product generation [21].

In pyrolysis, biomass converts into the liquid products operated in a single-step [22–27]. The subsequent fluid item contains an intricate combination of a range of compounds. The upgraded fractions from bio-oil are also referred as the 'drop-in' fuel or transportation fuel. There are different techniques been highlighted in literature for valorization of biomass to fuels and commodities [28,29]. For the utilization as a fuel,

there are various routes for bio-oil conversion such as hydrodeoxygenation and catalytic cracking. As per the published data, there is a higher amount of olefins and BTX being found in the bio-oil. However, due the uncertain nature of the bio-oil, it cannot be utilized as a fuel as it is [19,30,31]. Bio-oil has low cetane index and low energetic value. Fuel value is obtained by emulsification of bio-oil with mineral diesel, bio-diesel and bio-ethanol [31]. There are challenges associated with the catalytic processing of bio-oil for fuel value such as presence of phenols. In catalytic processing, carbon gets deposited on the catalyst and leads to catalyst deactivation and reactor plugging. Major route to get away from this problem is the addition of methanol to bio-oil. This not only stabilizes the oil but also reduces the lignin content, and thus there will be no deposition of the carbonaceous material over the catalyst. Another route is the catalytic processing of aqueous layer as it does not contain lignin composition and thus no catalyst deactivation. Though the biomass-based fuels are CO_2 neutral and comprises low sulphur content, presence of oxygenated compounds in the bio-oil, adds the undesirable property i.e. instability during storage over time. The high water and oxygen content makes bio-oil unsuitable for the utilization as a fuel [8]. Other challenges such as the poor volatility, high viscosity, coking and corrosiveness were faced by most of the authors [32]. The storage stability and fuel properties can be improved using up-grading and refining [21]. Q. Lu et al. [33] discussed about the ageing properties of bio-oil and found that methanol hinders the bio-oil from ageing [33]. The ageing is determined under accelerated ageing test by measuring viscosity and water content. The viscosity and water content of the bio-oil increases as the bio-oil ages. However, it was suggested that increase in viscosity is higher than increase in water content during aging process [34].

This review covers several technologies applied for the bio-oil upgradation and separation to value added chemicals. Fig. 1 describes overall separation techniques right from thermochemical conversion to value-added chemicals. When biomass is pyrolyzed, it basically converts to biogas, biochar and bio-oil, which is reviewed in literature. Biogas is further processed to gain fuel properties whereas biochar is utilized for improving fertility of soil. Our main area of focus for this review is bio-oil separation and upgradation. Chemicals such as acids, anhydrosugars, alcohols, aldehydes, ketones, esters, phenolics, pyrolytic lignin and furans are extracted using separation techniques. Some of the separated fractions are then upgraded for fuel value. The flowsheet in Fig. 1 describes two pathways to find value from the biomass. The upgradation route leads to the utilization as fuel value from techniques such as hydrotreating, deoxygenation, catalytic cracking, catalytic hydrogenation, steam reforming, esterification and emulsification. The separation technologies are being described particularly for the chemical value by techniques such as distillation, fractional condensation, liquid–liquid extraction, column chromatography, adsorption, crystallization, electrozorption, etc.

2. Bio-oil characterisation

Bio-oil characterization is one of the extensively studied areas in the last two decades [37–40]. Bio-oil comprises of various oxygenated compounds, including aldehydes, alcohols, esters, anhydrosugars, furans, carboxylic acids, water, phenols and ketones [37,38,41–46]. The composition of bio-oil depends on the process conditions during thermochemical operation. The compounds in bio-oil are not quite the same as those of oil from petroleum sources. It comprises of various mixtures from disintegration reaction of lignin, cellulose and hemicellulose. The mixtures in the bio-oil range from non-polar (e.g., hydrocarbons) to polar (e.g., phenolics) and from unstable (e.g., natural acids) to nonvolatile (e.g., sugar subsidiaries), covering an atomic weight (MW) of around 50–2000 Da. Subsequently, different procedures like high pressure liquid chromatography (HPLC), gas chromatography (GC), gel permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (NMR), and Fourier transform infrared spectroscopy (FTIR) are
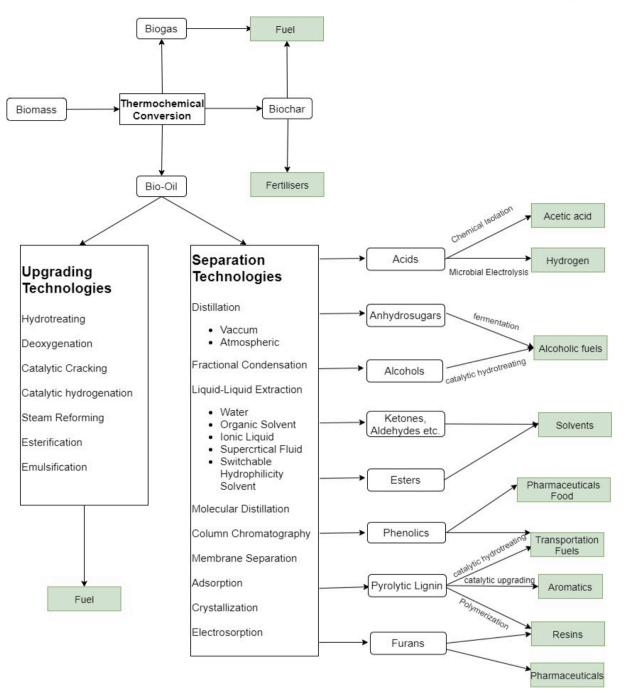
Fig. 1. Schematic overview of bio-oil separation and upgrading technologies [35,9,10,11,36,15]

needed to decide the bio-oil's structure [47]. There are several techniques available in the literature to analyze the components present in bio-oil. To measure the amount of water, authors have suggested Karl Fisher titration, near infrared spectroscopy and NMR. To analyze the amount of pyrolytic lignin, cold water precipitation is suggested. The analysis of aldehydes, ketones, acids, furans, esters, monosaccharides, anhydrosugars, aromatics, phenols, etc., categorized under C1-C10 light volatiles and semi-volatiles, are conducted by GC–MS and GC-FID. Aliphatic alcohols are analyzed by P-NMR. The carbohydrates and total carbohydrates are analyzed by solvent extraction, sulphuric acid-UV method and phenol- sulphuric acid acid-vis method. The hydrolysable sugars by HPLC-RID and IEC. Monosaccharides and anhydrosugars by C NMR, Faix, nicolaides titration and FTIR. Carbonyl compounds in which total carbonyls and individual aldehydes are characterized by C-NMR, Faix and nicolaides titration, FTIR, derivatization GC–MS and derivatization HPLC-UV. Carboxylic acids with total acids are characterized by C-NMR and TAN. Individual acids by SPME-GC–MS, derivatization GC–MS, derivatization HPLC-UV, derivatization LC-MS-MS and IEC. Phenols, categorized as total phenols and individual phenol, are analyzed by Folin-Ciocalteo method, PhAN, P NMR and LLE, and Derivatization GC–MS [47,48,49,42,10].

3. Bio-oil separation techniques

Different separation techniques have been reported in literature for separation of components from bio-oil mixture. These methods have been discussed in detail below:

3.1. Fractional condensation

Fractionation is a promising strategy that was applied to the separation of bio-oil fractions. Fractionation usually separates the bio-oil into two cuts called as the heavy and light fractions where the condenser operates at the decreasing temperature gradient [49]. During fractionation, the lighter fraction comprises water, C1-C4, mono phenols and mono sugars. The heavier fraction comprises oligomers in the form of aerosols [50]. Research has been published in reference to the fractionation of bio-oil to differentiate them into various fractions depending on differences in volatilities. To determine the final composition of the fractions, temperature, residence time, and condensation surface are the important parameters. Temperature of the reactor and the temperature of the first condenser play a critical role in the fractionation. Westerhof et al. [18] evaluated the effect of pyrolysis temperature and first condenser temperature (somewhere in the range of 25 °C and 70 °C) on the yield of bio-oil. The authors succeeded in separation of bio-oil rich in acetic acid, hydroxyl acetaldehyde, acetol and heavy oligomeric constitutes. The authors also have developed a numerical model for separated compounds which describes the yield of fractions. The model created by Westerhof et al. [51] has considered bio-oils as a combination of 13 gatherings each of which represents compounds with specified range of vapor pressures.

Table 1 is a comprehensive review of separation of bio-oil carried out by fractional condensation.

3.2. Distillation

Distillation is the process of separation of components from a mixture depending on the difference in boiling point and volatility. There have been more than 400 mixtures recognized in bio-oil which are formed through pyrolysis of biomass. There are various distillation techniques such as molecular distillation, vacuum distillation and atmospheric distillation which are being illustrated for the recovery of compounds from bio-oil.

3.2.1. Atmospheric distillation

Atmospheric distillation is one of the techniques to produce chemicals from pyrolysed bio-oil with zero waste production. As the temperature in atmospheric distillation increases to 250 °C, reaction between the components leads to production of water. In atmospheric distillation, acids, alcohols and aldehydes are more favourable than the phenols due to their instability in heating process [63]. The range of atmospheric distillation of bio-oil compounds is between 80 and 250 °C leaving around 40% of the residue. Heating the bio-oil during atmospheric distillation also leads to reaction between the components which leads to ageing of bio-oil [33].

3.2.2. Conventional vacuum distillation

Vacuum distillation operates at much lower temperatures than the atmospheric distillation. Although vacuum distillation takes a lot more of energy, the organic fractions contains no water and fewer oxygenated compounds. This helps the fractions from getting aged and unstable. In comparison to the atmospheric distillation the residues are very limited in vacuum distillation of the mixture of components [33].

3.2.3. Molecular distillation

Molecular distillation, also called the short path distillation, is a process in which thermally unstable and closed boiling components are separated under a high vacuum. This separation technique relies on the differences in free paths of different substances [16]. Molecular distillation is the most preferred separation technique as it is suitable for thermally unstable materials. Compared to other distillation processes, molecular distillation obtains more yield in bio-oil distillates. Other refining measures experience the ill effects of the issues of coking at higher temperature and low yield.

Table 1
Fractional condensation of bio-oil.

Bio-oil source	Condenser Temperature (°C)	Findings	Ref.
Cotton stalk	300 °C, 100 °C, 0 °C and −20 °C	Separated 90 % of the water and organic acid content in the third condenser	[52]
Rice husk	110	Separated fraction composed of phenolic products	[53]
Pine dust	96–110	23.3–29.8 wt% dry oil	[53]
	82	2.4–4.4 wt% water content 2.92 wt% bio-oil	
Nordic wood	80	Lignin derived	[54]
	60	Water, sugars, alcohols, hydrocarbonyls and acids	
	4	Water, aldehydes, ketones and acids	
Stem wood	258	2-6 wt% water, LMM and HMM lignin and extractives	[55]
	258–159	2–6 wt% water, LMM and HMM lignin and extractives	
	73	36–42 wt% water, anhydrosugars, anhydrooligomers and hydroxy acids	
	coalescing filters	2–6 wt% water, LMM and HMM lignin and extractives	
	5	50–53 wt% water, aldehydes, ketones, acids, alcohols and lignin monomers	
Birch bark/ BFB	105	Dry oil	[56]
	<15	Aqueous waste	
Red oak/ FB	102	Dry oil	[57]
	77	Next dry oil	
	18	Aqueous waste	
Pinewood/ FB	115	Dry oil	[11]
	Coolant at 20	Aqueous waste	
Kraft lignin/ BFB	105	Dry oil	[36]
	<15	Aqueous waste	
Acacia tortilis, Pyrolyzed in a bench-scale plant	140	Oil fraction with a heating value (HHV) of 36.807 MJ/ kg 41.9% yield pH value of 3.42	[58]
Pine dust, Pyrolyzed in a bench-scale plant	110	Oil fraction with a heating value (HHV) value of 15.78 MJ/kg 46.1% yield pH value of 2.50	[58]
	0 °C	Water-rich product	
Black spruce wood, Fast pyrolysis	120 °C	Reduced water in the oil phase	[59]
	80 °C	Prevent water and light carboxylic acids from condensing in the oil phase	
Pyrolysis with spray condensers and an intensive cooler in series	70 °C – 90 °C	Heavy oil fraction; 20% saccharides and 40% lignin oligomers 10–4% water and around 3–2% acetic acid	
Red oak, Fluidized bed reactor	129 °C	Reduced the content of water and acidity in bio-oil Enriched concentration of anhydrosugars, lignin oligomers Recovered 85% of the total bio-oil energy	[60]
Rice husk, Fixed bed pyrolysis	110	Abundant phenolic compounds	[61]
	0	medium-boiling compounds with relatively high concentrations of water, acids, and ketones	
	−196	hydrocarbons and water	
	≤80 °C		[10,35]

(continued on next page)

Table 1 (*continued*)

Bio-oil source	Condenser Temperature (°C)	Findings	Ref.
Batch pyrolysis of Corn stover Fluidized bed pyrolysis of cotton stalk		26.6% yield (10.3% organic layer) (16.2.% water layer)	
Lab batch pyrolysis of Walnut shells	80–160 °C	5.9 % yield	[62]

Several studies with molecular distillation have been reported for the separation of bio-oil fractions. Bio-oil from biomass fluidized-bed flash pyrolysis was fractionated using molecular distillation into light (LF), middle (MF) and heavy (HF) fractions [66]. Molecular distillation technology can effectively separate acid compounds and hence reduce the pH value of bio-oil without coke formation. Water is also separated from the crude bio-oil by molecular distillation at a temperature as low as 50 °C [16]. Table 2 describe the technique of molecular distillation and products obtained at the particular conditions.

Table 2

Molecular distillation of bio-oil

Bio-oil source	Pressure	Temp range	Findings	Ref
Mongolian pine sawdust	100 Pa	80 °C	Yields: 50, 6.75, 40.9 wt% of light, middle and heavy fractions respectively	[64]
Mongolian scotch pine	60 Pa	70, 100 and 130 °C	Yields: 83 wt% of distillates	[65]
Lauan sawdust	120 Pa	70 °C	Yields: heavy fraction 49.58 wt% Yield: 19.88 wt% pyrolytic lignins in the heavy fraction	[9]
Softwood and bark bio-oils	Under vacuum (10 kPa) for 0.5–1 h	60–100 °C	Methanol and acrolein distilled completely, acetic acid and acetol failed could not be distilled after 1 h	[66]
Woody bio-oil		LF at 30–150 °C HF at 450 °C	LF contained mainly water (70%) and acids with a low boiling point temperature; main products obtained were water, CO2 and alcohol, MF contained water, formic acid, and some CO and CH4 and HF contained alcohols or phenols and CO2	[64]
Biomass	1600 Pa	80 ○C	26.36% (w/w) rich in low molecular weight carboxylic acids and ketones	[15]
	340 Pa	80 ○C	22.58% (w/w) rich in low molecular weight carboxylic acids and ketones	

3.3. Liquid- liquid extraction

Various extraction strategies have been studied to separate bio-oil into unique fractions or to separate a particular compound from a bio-oil mixture. These methods include water extraction, extraction using organic solvents (sequential or combined), reactive liquid–liquid extraction, switchable hydrophilicity solvent extraction, supercritical fluid extraction, and ionic liquid extraction. Fig. 2 is a detailed scheme for bio-oil separation by liquid–liquid extraction method. The scheme is drawn for both water soluble and insoluble compounds.

3.3.1. Water extraction

Water extraction is a promising strategy to separate the water-dissolvable and water-insoluble portions. Numerous studies have reported that the addition of 25–35% of water into the bio-oil generate two phases. These two generated phases are having components as per their solubilities. One such stage is the heavy tar-like phase rich in lignin-determined mixtures and the other stage is a watery stage rich in cellulose and hemicellulose derivered compounds [70]. Water extraction is often considered as the essential technique for the recovery of chemicals from bio-oil [71]. Vitasari et al. [71] have conducted extraction of the bio-oil generated from the forest residues feedstock and recommended that the proportions for extraction to be kept at a mass water-to-oil ratio of 0.65–0.7 and for the pine-derived oil at 0.5. Based on the polarity of the bio-oil, about 80–90% of the oxygenated compounds can be extracted to the watery stage, upon water addition to the pyrolysed oil. Oasmaa et al. [40] have investigated that a different stage was formed at the point when water was added to bio-oil, thus found that bio-oil phase stability (the formation of oil and aqueous phases) is controlled by the relative quantities of lignin oligomers (water-insoluble materials), water, sugars and light C1 – C4 molecules that act as solvents. Park et al. [72] have contemplated the separation of bio-oil fractions by adding the oil – water, organic solvents (hexadecane and octane), and sodium hydroxide and concluded that a biphase fluid/ natural separation happens as the pH increases. Table 3 is a brief review on the findings of water extraction studies of bio-oil from the published literature.

3.3.2. Organic solvent extraction

Organic solvent extraction is extensively studied in the literature [13,77–79]. Solvent extraction is a process in which targeted components from a mixture are selectively extracted having greater affinity into a solvent. The solvents that are commonly used for extraction are water, alcohols, ethyl acetate, diethyl ether, n-hexane, octane, chloroform, dichloromethane, carbon tetra chloride, etc [39,54–63]. Organic solvent extraction create two phases, one is the solvent-soluble, and another is the non-soluble phase. Commonly two methods are reported in the literature: one depends on the polarity of the fractions and the other is an acid-base separation. The boiling point of the solvent also plays a key role in the extraction technique. The solvent-soluble fraction in the pyrolysis oil-rich phase is another parameter that needs to be carefully considered when developing liquid – liquid extraction strategy. Table 4 is an overview of the research findings in which fractions were recovered by organic solvent extraction. Organic solvents are least soluble in water. Organic solvents with non-polar behavior such as the hexane, ethyl acetate, petroleum ether and chloroform have the highest tendency to recover compounds. Chloroform has highest extraction efficiency for furans, phenols, and ketones, whereas ethylacetate has highest extraction efficiency for organic acids. When the chloroform and ethyl acetate are used in step wise manner for extraction, they have tendency to recover ketones, furans, alcohols and phenolics. Higher concentration of levoglucosan also gets extracted from the aqueous phase by the use of ethyl acetate [75].

3.3.3. Switchable hydrophilicity solvent extraction

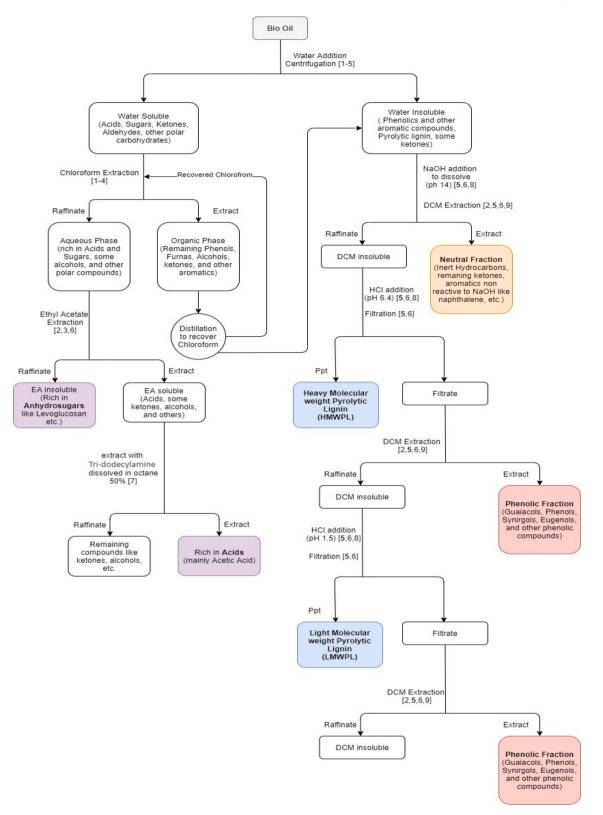Switchable solvents are those which can reversibly change their

Fig. 2. Bio-oil separation scheme [67,13,68,69,49]

properties upon application or expulsion of a trigger (regularly CO_2). Switchable Hydrophilicity Solvents (SHSs) can hence be defined as solvents that can switch reversibly between one form that is miscible with water in the absence of CO_2 to another that forms a biphasic mixture with water in the presence of CO_2. Fu et al. [36] examined the extraction of phenol from microwave-pyrolysed bio-oil utilizing N,N-

dimethylcyclohexylamine as the switchable hydrophilicity solvent. They obatined a concentrated phenolic fraction with 72% of guaiacol and 70% of 4-methylguaiacol in the crude bio-oil recovered with just a 9% solvent loss [36].

Table 3
Water Extraction Studies of bio-oil

System	Bio-oil source	Findings	Ref
Batch stirring	Forest residue-derived pyrolysis oil	Recovery of 80–90% of polar components	[71]
Water addition	Auger pyrolysis of switchgrass	Recovery of acids, alcohol, furan, ketone, phenol, sugar.	[72]
Water addition	Fast pyrolysis of Hardwood and softwood lignin	Acids, ethers, phenolic, and aromatics were separated	[73]
Water addition (1:1-water: Bio-oil) + Centrifugation	Microwave pyrolysis of douglas fir pellets	61.82 wt% of total organics in the water phase. Oil phase organic concentration reaches 90%	[17]
Water addition (41% water)	–	70–80% aromatics enriched in paste like phase. Sugar derivatives as main components in water phase	[74]
Water addition (4 times bio-oil volume)	Fast pyrolysis of switchgrass	Water phase rich in levoglucosan and acids	[75]
Dropping bio-oil into ice-cooled distilled water (1,000 ml Water-to-oil ratios 5 : 1, 10 : 1, 15 : 1 and 20 : 1 by volume	Slow-pyrolysis	The coming about pyrolytic lignin had a remarkably higher warming worth, lower corrosiveness, higher soundness, and subsequently greater, than the beginning bio-oil	[44]
Water addition (1:1-water: Bio-oil)	Fluidized bed pyrolysis of lauan sawdust	Yield: phenolic compounds = 94.35%, guaiacols = 48.27%	[76]

3.3.4. Supercritical fluid extraction

Supercritical fluid extraction (SFE) is usually accompanied by CO_2 as a solvent. Recently, a lot of advancements have been made in the field of supercritical fluid extraction. Different solvents have been studied for their potential use as Supercritical fluid extraction (SFE) solvent. CO_2 is most commonly used because it is non-toxic, non-flammable and fairly inexpensive [82,83]. Reported literature suggests that CO_2 is mainly used for the extraction of hydrophobic components. The advantage of supercritical CO_2 extraction over the organic solvent-based extraction is that it has higher affinity towards hydrophobic constitutents. This method also allows continuous modulation of the selectivity and extraction efficiency. This makes it more flexible than conventional extraction methods. Moreover, this method does not require polluting organic solvents and thus no efforts on their removal [7]. The selectivity of the components as per requirement can be altered by changing the pressures and temperatures. The significant drawback is that it requires high pressure to achieve its supercritical state. It also requires higher operating cost compared to other methods of extraction such as the liquid–liquid extraction. Cheng et al. [84] carried out supercritical fluid extraction of red pine bio-oil. They conducted the experiment in three stages: the first stage comprised of pure CO_2 at 10 MPa pressure for 5 min, the second stage with 90% CO_2 and 10% methanol at 20 MPa pressure for 25 min and the third stage with 75% CO_2 and 25% methanol at 30 MPa pressure for 40 min. Various chemical components were extracted with percent yield of 13.4%, 24.8% and 32.9% in first, second and third stage respectively. Feng and Meier [85] conducted supercritical fluid extraction of beech wood at 60 °C operating temperature and 20 MPa pressure.

3.4. Membrane separation

Membrane separation, such as microfiltration (0.05–10 μm), ultrafiltration (1–100 nm), and nanofiltration (<2 nm), have been utilized for bio-oil fractionation. Membrane separation for the separation of bio-oil has advantages and disadvantages. The separation of each constituent with respect to the feed composition is one of the key factors. Affinity separation is recommended when the products and medium show significant differences in acidity/basicity, polarity and H-bonding. It is also recommended when the interactions are not too weak or too strong, and when there is a path for affordable sorbent recovery. Permeation is suggested in the literature at the point when the product and medium have large differences in molecular weight and when affordable permeable materials are available.

3.5. Column chromatography

The separation of bio-oil using column chromatography is a viable procedure to get refined mixtures separately. Generally, silica gel, aluminum oxide and macro-porous adsorbent resin are utilized as the stationary phase. Their selection is based upon the polarity of bio-oil components which are to be extracted. Separation depends on various adsorption abilities of bio-oil segments onto the stationary phase. Column chromatography can economically separate bio-oil, but its low throughput makes it only suitable for high value-added compounds. In one investigation, it was found that hazardous phthalate esters could be separated from bio-oil using column chromatography [86]. The method of column chromatography is linked with methods such as pre-treatment, dehydration, extraction and concentration. In a study, column chromatography was used to enrich bio-oil fractions [87]. The results show that C8-C30 alkanes were advanced in petroleum elution sub-fractions with a concentration of 97.6%. Phenols were efficiently enriched in high concentration ~ 100 % by elution of acetone/carbon disulfide. Column chromatography has many benefits over other separation methods in terms of low energy consumption, high efficiency, easily achievable conditions, and environmental substantiality.

3.6. Electrosorption

Electrosorption, also known as capacitive deionization (CDI) is a new approach used for extraction of acids from aqueous phase of bio-oil. A study used electrosorption to separate acetate and propionate ions from water soluble fraction of switchgrass bio-oil and convert them into hydrogen with 80–90% efficiency [72]. Another set of experiments conducted by Andersen et al. [88] used electrolysis to extract carboxylate which are further passed through an ion exchange membrane to form concentrated carboxylate solution.

4. Application of fractions achieved after separation

Bio-oil contains number of fractions namely acids, anhydrosugars, alcohols, ketones, aldehydes, esters, phenols, pyrolytic lignin, furans, etc. Pinheiro Pires et al. [89] revealed that mixture of bio-oil can be blended with alcohols to improves the fuel properties. They additionally suggested that bio-oil blended with methanol and tetra (ethylene glycol) dinitrate compound makes bio-oil appropriate to be utilized in high velocity diesel motors as it improves cetane number. In addition, it was also reported that water soluble fractions are blended with glycerol. This decreases the acidity and water content, and increases the heating value and density of water soluble fuels [89].

Authors have suggested that due to the high water and oxygen content in bio-oil, it can not be utilised directly. There is a need to upgrade the fractions to high grade liquid fuels. This is another aspect of application than just the chemical value. Upgrading techniques such as the hydrogenation, cracking, esterification, emulsification and steam reforming are major techniques reported in the literature. After separation, most unsaturated compounds such as the aldehydes, ketones and alkenyl compounds that influence the storage stability of bio-oil are treated by hydrogenation. This improve its overall saturation and utilisation as a high quality liquid fuel. This is one of the expensive methods for creating fuel value from the bio-oil. Catalytic cracking helps to remove oxygen from the compounds, which can then be utilised as high

Table 4
Organic solvent extraction studies of bio-oil

System	Bio-oil source	Solvent	Findings	Ref
Aqueous phase fractionation	Pyrolysis of softwood bark	Toluene	The phenolic fraction was separated	[13]
Solvent extraction	Auger pyrolysis of switchgrass	Ethyl acetate	Recovery of acids, alcohol, furan, ketone, phenol, sugar, ether and alkane	[72]
Solvent extraction	Fast pyrolysis of Hardwood and softwood lignin	Toluene Methanol	Phenolic and aromatics were separated Phenolic, esters and aromatics were separated	[73]
Solvent extraction	Microwave pyrolysis of douglas fir pellets	Chloroform	At a 1:2 proportion of bio-oil to dissolvable total of 73.84% organics were extracted in the chloroform phase	[17]
Acid catalysis coupled with solvent extraction		Chloroform	Acid treatment converted sugars to levulinic acid/esters and chloroform shows over 90% extraction efficiency for them	[74]
Sequential Solvent Extraction		Chloroform and Ethyl acetate	62.2 wt% of unique furans, ketones, alcohols, and phenolics extricated into chloroform while 62 wt% acidic corrosive removed into ethyl acetic acid derivation leaving behind a high centralization of levoglucosan (~53.0 wt%) in the last watery stage	[75]
Two stage Solvent Extraction	Pyrolysis of Coconut shell	First stage – Distilled Water + Chlorofom (4-5℃) Second Stage – Methanol (50℃)	94.89% phenol extraction to methanol with a distribution co-efficient of 7.29.	[69]
Reactive Extraction of Phenols	Pyrolysis of Coconut Shell	Ethyl Ether and NaOH followed by neutralization using HCl	Separated of Phenolic compounds from bio-oil	[80]
Solvent extraction for phase separation	Pyrolysis of Jatropha Curcas seed cake	Salt addition and Centrifugation Organic Phase extraction with Hexane Extraction of organics from aqueous phase using Ethyl acetate	Separation into three phases: Organic Phase rich in hydrocarbons Aqueous phase rich in acids and aldehydes Polymeric phase rich in heavy weight compounds	[68]
Combined extraction Sequential extraction		Octane and Hexadecane	Combined Extraction is more effective in extraction of chemicals specially phenols	[72]
Sovent extraction and pH alteration	Pyrolysis of bio-oil waste	Water, Ethyl acetate, Hexane.	Addition of NaOH improves extraction efficiency. Separation into three phases: Hexane phase rich in methyl esters; EtAc phase rich in phenol derivatives; Aqueous phase rich in acetic acid	[67]
Multi-step solvent extraction		Dichloromethane as Solvent. NaOH for pH alteration. HCl for neutralization	Five different fractions obtained: 2 phenolic fractions with 94.35% and 54.33% phenolic contents respectively. A heavy molecular weight pyrolytic lignin fraction A low molecular weight pyrolytic lignin fraction A neutral fraction with hydrocarbons inert to NaOH	[81]
Distilled water: bio-oil by weight at 4:1 followed by solvent extraction using chloroform and ethyl acetate	Pyrolysis Air-dried switchgrass (Panicum virgatum L)	Phase separation by water followed by extraction using chloroform and ethyl acetate	Yield: 62.2 wt% of original furans, ketones, alcohols, and phenolics into chloroform, while 62 wt% acetic acid into ethyl acetate	[47]

grade liquid fuels.

4.1. Products from bio-oil phenolic fraction

Phenolic compounds have a wide range of uses. Basic phenols can be utilized in numerous industries like chemicals, pharmaceuticals, food processing and resin manufacturing. Jo-Sik Kim [90] suggested that phenolic-rich bio-oils are great replacement to phenol sourced from fossil fuels. Capunitan and Capareda [10] expressed that phenols can also be used in the adhesives and speciality polymers industry.

4.2. Products from bio-oil heavier fraction

As the heavier fraction carries good heating value and its elemental composition is almost similar to the diesel, it can be emulsified with diesel for fuel value utilization. Bertero et al. [11] suggested emulsification of pyrolysed oil with diesel for using as a fuel in low-speed engine. NO$_x$ emissions were 50% less with emulsified oil. One other application of heavy fractions is utilization as fuel in heater or kettle frameworks. Upgradation of the heavy fraction can be carried out in crude oil refinery, typically it is called feedstock to the crude oil refinery [91]. Heavy fraction also have wide applications in flavourings, agrichemicals, resins, fertilizers and as emission control agents. Thus, this fraction is also called as the best mixing material with other liquid fills [10].

4.3. Products from bio-oil fraction mixtures

Pires et al. [6] highlighted formation of calcium salts with lime using carboxylic acids and phenols. This can be utilized for adsorption of acid gas compounds like SOx. In their work, they also suggested that slow release nitrogen fertilizers can be produced from the reaction of carbonyl, carboxyl, hydroxyl, phenolic and methoxy bio-oil functional groups. This helps to produce less pollution in groundwater as compared to the mineral fertilizers. This also contains humic type material (lignin) which is used as a conditioning agent to the soil.

5. Limitations and knowledge gap

Bio-oil lacks in refining capability and thus does not allow

deployment of the bio-oil upgrading technology in plants. Thermal stability is one of the drawback during not only upgrading but while storage and handling. As bio-oil contains more than 40% water and thus refining costs are higher for bio-oils than petroleum fuels. Table 5 shows limitation over some techniques of bio-oil separation.

6. Techno-economic assessment

Bio-based chemicals have acquired more widespread attention than bio-fuels in view of the decrease in petroleum costs. The advancement of technologies to create chemical compounds from bio-oil is potentially attractive due to simplicity in bio-oil generation. This study presents a prospective and detailed techno-economic life-cycle assessment.

Zhang et al. [92] proposed two pathways for bio-oil upgradation which included two-stage hydrotreating followed by fluid catalytic cracking (FCC) and single-stage hydrotreating followed by hydrocracking. In the hydrotreating/FCC pathway, two choices are open as the hydrogen focal point for hydrotreating transporter hydrogen and hydrogen from petrol gas changing. The fundamental aftereffects of the hydrotreating/FCC pathway are product fabricated materials, however the fundamental aftereffects for the hydrotreating/hydrocracking pathway are transportation forces and hydrogen. The pathways can be exhibited using Aspen Plus for the techno-economic assessment. A 2000 metric tons/day basis was considered. Calculations for equipment assessment and cost were conducted using Aspen Economic Evaluation program. They have suggested that the internal rate of return (IRR) for every pathway as a function of feedstock cost, fixed capital investment (FCI), hydrogen and driving force costs, and office wages can be examined by Aspen Economic Evaluation programming. They also have discussed brief assumptions of the capital cost estimation for installation of a plant, estimation of commodity and feedstock for evaluation of the process. A correlation between the commodity chemicals and petroleum prices have been discussed. Since the market costs of items are unstable especially for energy items, a presumption with upto 20 years of cost assessment is proposed while doing financial assessment. They also suggested that all the calculations should be a segment of yearly livelihoods, fixed capital endeavour and yearly working costs. The advancement has been believed to be grown enough as indicated by the perspectives of steadfast quality and execution to ensure that the workplace fills in as a nth plant instead of as a pioneer plant. Affectability investigation has additionally been performed to decide the affectability of the office's monetary practicality to the model boundary esteems for the two pathways. An outline of their work suggests that hydrogen cost, fixed capital expense, feedstock cost and product yield are vital elements in the monetary plausibility of the two bio-oil overhauling pathways [92].

Sorunmu et al. [93] compared performance of the alternative pathways for bio-oil upgradation. They suggested that for fuel commercialization pathway, minimum fuel selling price is always considered. Considering the average cost in the market for gasoline and diesel, they have embarked and concluded that most of the literature on the cost of

fuel pathways have exceeded the minimum fuel selling price. However, few have reached their limit. Their study had proved that the pathway with hydrodeoxygenation had reached their limit to minimum fuel selling price according to the market. The work concluded that the modestly set tax would not let the bio-oil upgrading pathways to reach the minimum fuel selling price excluding for the hydrodeoxygenation pathway [93]. Zheng et al. [94] have introduced the techno-economic and environmental assessment on integrated bio-refinery process which combined fast pyrolysis, fractional condensation of bio-oil vapours and respective extraction of three chemicals for the full utilization of bio-oil fractions. For the quantification of techno-economic feasibility total-capital investment, equipment cost, direct production cost and operating costs were estimated and the internal rate of return for 20 year facility was calculated. Best computation apparatus for monetary appraisal and their properties as proposed by them are Aspen Process Economic Analyser (APEA) and SuperPro Designer for assessment of capital expense, working expense and speculation income bends for assessment of lifecycle financial effect of interaction plans during calculated plan. For saving time and eliminating errors caused when physically moving information between measure plan and assessment divisions coordinated interaction test systems Aspen HYSIS and Aspen Plus are recommended by them. They additionally gave a light on the distinction in activity application by Aspen and SuperPro Designer wherein financial assessment and enhancement of incorporated cycles in a wide scope of industry measures, like drug, biotech, strength mineral preparing, microelectronics, water decontamination, wastewater treatment, air contamination control can be just done by SuperPro Designer and clarified that Aspen needs for successful displaying for these enterprises [94].

Maqbool et al. [95] discussed about economic assessment by Aspen Process Economic Analyser used with Aspen for the four process design scenarios. The economic cost was assessed by them from the total capital cost as done by Zheng et al. in their paper [94], raw material or feedstock cost, utilities and operating cost and annual product sales and profit. In this manner to ensure economic competitiveness bio-oil prices efforts are needed to keep bio-oil production costs lower to $150 t-1 [89].

As of now, a cost-effective pathway has not been achieved for bio-fuels production from pyrolysed bio-oil. The thermochemical upgrading technologies for bio-oil are similar to petroleum refinery approaches. However, due to the presence of water and oxygen content in bio-oil, it is incompatible with the existing infrastructure of petroleum refinery. Hence, bio-oil upgradation also requires stabilization as a technique for long term applications [91]. As per the need of bio-oil as fuel, some changes should be managed for large scale valorization of the different feedstock. To reduce the cost of production of fuels from the bio-oil sources, the existing technologies can be utilized for achieving desired goals. This will reduce the infrastructure cost and problems associated with manufacturing and product refining. Further, for the long term investment, there is a need to redesign and implement new units for upgrading raw bio-oil and its mixtures [96].

Bio-oil can be considered as an economic fuel which is synthesized after the separation of pyrolysis oil. Hu and Gholizadeh [97] have carried out cost estimation for production of pyrolysisoil, separation, and upgradation to fuel. They confirmed the feasibility of bio-oil use as source of energy production [97]. Finally, with lower production costs, bio-oil may progress towards sustainable refineries with reduced net CO_2 emissions.

7. Summary and conclusion

The innovation of fast pyrolysis has been the promising course for change of lignocellulosic biomass to bio-oil. The commercial model of the bio-oil refinery facility does not come into existence because of its intricate nature. Each technology reported for the bio-oil separation has its own advantages and disadvantages. Parametric comparison for each

Table 5
Limitations are recognized with the following techniques in bio-oil [5]

Sr. no.	Technique	Limitation
1	Centrifugation	Homogeneous bio-oil
2	Atmospheric and vacuum distillation	Thermo-sensitive bio-oil
3	Flash and steam distillation	1. Suitable for pre-separation. 2. Limited to laboratory and difficult to scale-up.
4	Molecular distillation	1. Bio-oil is complex mixture. 2. Effectively goes through responses like disintegration, polymerisation and oxygenation. 3. Thermo-sensitive.

method is summarized. In case of fractional condensation, there is specified range for fractions which are expected to be found in that particular condensation temperature range. Phenolics at 110 °C, lignin derived components at around 80 °C, water, sugars, alcohols, hydrocarbonyls and acids at around 60 °C, water, aldehydes, ketones, and acids at around 4 °C and atmospheric pressure. Fractional condensation is a promising method of bio-oil separation and is cost effective. Water based extraction leads to phenol and lignin separation when the amount of bio-oil and water used are either equal in concentration or water higher than the bio-oil. The phases get separated for conventional extraction practices. Levoglucosan, acids, sugar derivatives and aromatic enriched phases are separated in water extraction. Other than the operating cost of extraction, water is needed to be removed at the final stage which does not need much cost as it only requires evaporation. Solvent extraction aids in extracting phenols by the use toluene, ethyl acetate and dichloromethane. The comparative study of the solvent extraction in literature suggests that each solvent has tendency to solubilize particular group of components. Toluene recovers mainly phenolic fractions. Ethyl acetate recovers acids, alcohol, furan, ketone, phenol, sugar, ether and alkane. Methanol mainly recovers phenolic, esters and aromatics. Likewise, chloroform and ethyl acetate together recovers furans, ketones, alcohols and phenolic altogether. Organic solvent extraction has higher affinity towards extraction of majority of the compounds. This is an effective method as compared to water extraction in terms of efficiency.

Solvent extraction and distillation are the most conventional methods of bio-oil separation. This is due to extraction of the dominant fractions present in bio-oil. Phenolic family, which is dominant in concentration in many of the bio-oils, solvent extraction followed by distillation can be used for separation. From the overall review contingent upon the volatility differences of the bio-oil compounds, VLE studies lead by fractional distillation is another promising technology for separation. Most of the products that are separated by this method are acids, phenols, guiacols, ketones, catechols and their derivatives. These chemicals bear widespread applications into the industrial markets.

Out of atmospheric distillation, vacuum distillation and the molecular distillation reviewed, molecular distillation is the most efficient for bio-oil separation. Atmospheric distillation has drawbacks in terms of efficiency. Molecular distillation which operates in step wise manner is highly efficient and cost effective. Extraction followed by distillation is the preferred method to separate out chemicals of interest. Extraction can separate a family of compounds and those family of compounds can be separated in each fraction depending on their boiling point differences. Both the techniques; the solvent extraction and molecular distillation are operated at the lower costs with the higher efficiencies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

References

[1] S.H. Chang, Bio-oil derived from palm empty fruit bunches: Fast pyrolysis, liquefaction and future prospects, Biomass and Bioenergy 119 (April) (2018) 263–276, https://doi.org/10.1016/j.biombioe.2018.09.033.

[2] H. Kobayashi, A. Fukuoka, Synthesis and utilisation of sugar compounds derived from lignocellulosic biomass, Green Chem. 15 (7) (2013) 1740–1763, https://doi.org/10.1039/c3gc00060e.

[3] M. Bhatt, et al., Valorization of solid waste using advanced thermo-chemical process: A review, Journal of Environmental Chemical Engineering 9 (4) (2021), https://doi.org/10.1016/j.jece.2021.105434.

[4] Z. Si, X. Zhang, C. Wang, L. Ma, R. Dong, An overview on catalytic hydrodeoxygenation of pyrolysis oil and its model compounds, Catalysts 7 (6) (2017) 1–22, https://doi.org/10.3390/catal7060169.

[5] D.E. Resasco, S.P. Crossley, Implementation of concepts derived from model compound studies in the separation and conversion of bio-oil to fuel, Catal. Today 257 (P2) (2015) 185–199, https://doi.org/10.1016/j.cattod.2014.06.037.

[6] Y. Han, A. Paiva, P. Pires, M. Denson, A. G. Mcdonald, and M. Garcia-perez, "Ternary Phase Diagram of Water / Bio-Oil / Organic Solvent for Bio-Oil Fractionation," 2020, doi: 10.1021/acs.energyfuels.0c03100.

[7] E. Reverchon, I. De Marco, Supercritical fluid extraction and fractionation of natural matter, J. Supercrit. Fluids 38 (2) (2006) 146–166, https://doi.org/10.1016/j.supflu.2006.03.020.

[8] S.S. Lam, E. Azwar, W. Peng, Y.F. Tsang, N.L. Ma, Z. Liu, Y.-K. Park, E.E. Kwon, Cleaner conversion of bamboo into carbon fibre with favourable physicochemical and capacitive properties via microwave pyrolysis combining with solvent extraction and chemical impregnation, J. Clean. Prod. 236 (2019) 117692, https://doi.org/10.1016/j.jclepro.2019.117692.

[9] Y. Wang, S. Wang, F. Leng, J. Chen, L. Zhu, Z. Luo, Separation and characterization of pyrolytic lignins from the heavy fraction of bio-oil by molecular distillation, Sep. Purif. Technol. 152 (2015) 123–132, https://doi.org/10.1016/j.seppur.2015.08.011.

[10] J.A. Capunitan, S.C. Capareda, Characterization and separation of corn stover bio-oil by fractional distillation, Fuel 112 (2013) 60–73, https://doi.org/10.1016/j.fuel.2013.04.079.

[11] M. Bertero, G. De La Puente, U. Sedran, Fuels from bio-oils: Bio-oil production from different residual sources, characterization and thermal conditioning, Fuel 95 (2012) 263–271, https://doi.org/10.1016/j.fuel.2011.08.041.

[12] D.S. Scott, J. Piskorz, The flash pyrolysis of aspen-poplar wood, Can. J. Chem. Eng. 60 (5) (1982) 666–674, https://doi.org/10.1002/cjce:v60:510.1002/cjce:5450600514.

[13] D. Mourant, D.Q. Yang, X. Lu, C. Roy, Anti-fungal properties of the pyroligneous liquors from the pyrolysis of softwood bark, Wood Fiber Sci. 37 (3) (2005) 542–548.

[14] L. Leng, H. Li, X. Yuan, W. Zhou, H. Huang, Bio-oil upgrading by emulsification/microemulsification: A review, Energy 161 (2018) 214–232, https://doi.org/10.1016/j.energy.2018.07.117.

[15] Z. Guo, S. Wang, Y. Gu, G. Xu, X. Li, Z. Luo, Separation characteristics of biomass pyrolysis oil in molecular distillation, Sep. Purif. Technol. 76 (1) (2010) 52–57, https://doi.org/10.1016/j.seppur.2010.09.019.

[16] Z.G. Guo, S.R. Wang, Y.Y. Zhu, Z.Y. Luo, K.F. Cen, Separation of acid compounds for refining biomass pyrolysis oil, Ranliao Huaxue Xuebao/Journal Fuel Chem. Technol. 37 (1) (2009) 49–52, https://doi.org/10.1016/s1872-5813(09)60010-4.

[17] Y.i. Wei, H. Lei, L.u. Wang, L. Zhu, X. Zhang, Y. Liu, S. Chen, B. Ahring, Liquid-liquid extraction of biomass pyrolysis bio-oil, Energy and Fuels 28 (2) (2014) 1207–1212, https://doi.org/10.1021/ef402490s.

[18] R.J.M. Westerhof, D.W.F. Brilman, M. Garcia-Perez, Z. Wang, S.R.G. Oudenhoven, W.P.M. van Swaaij, S.R.A. Kersten, Fractional condensation of biomass pyrolysis vapors, Energy and Fuels 25 (4) (2011) 1817–1829, https://doi.org/10.1021/ef2000322.

[19] S.S. Lam, P.N.Y. Yek, Y.S. Ok, C.C. Chong, R.K. Liew, D.C.W. Tsang, Y.-K. Park, Z. Liu, C.S. Wong, W. Peng, Engineering pyrolysis biochar via single-step microwave steam activation for hazardous landfill leachate treatment, J. Hazard. Mater. 390 (2020) 121649, https://doi.org/10.1016/j.jhazmat.2019.121649.

[20] S. Naik, V.V. Goud, P.K. Rout, A.K. Dalai, Supercritical CO2 fractionation of bio-oil produced from wheat-hemlock biomass, Bioresour. Technol. 101 (19) (2010) 7605–7613, https://doi.org/10.1016/j.biortech.2010.04.024.

[21] K. Jacobson, K.C. Maheria, A. Kumar Dalai, Bio-oil valorization: A review, Renew. Sustain. Energy Rev. 23 (2013) 91–106, https://doi.org/10.1016/j.rser.2013.02.036.

[22] A. Tumbalam Gooty and F. Berruti, "Fractional Condensation of Bio-oil Vapors," no. December, p. 92, 2012, [Online]. Available: http://ir.lib.uwo.ca/etd/979.

[23] J. Yip, M. Chen, Y.S. Szeto, S. Yan, Comparative study of liquefaction process and liquefied products from bamboo using different organic solvents, Bioresour. Technol. 100 (24) (2009) 6674–6678, https://doi.org/10.1016/j.biortech.2009.07.045.

[24] S.S. Lam, W.A. Wan Mahari, N.L. Ma, E. Azwar, E.E. Kwon, W. Peng, C.T. Chong, Z. Liu, Y.-K. Park, Microwave pyrolysis valorization of used baby diaper, Chemosphere 230 (2019) 294–302, https://doi.org/10.1016/j.chemosphere.2019.05.054.

[25] W.A. Wan Mahari, C.T. Chong, C.K. Cheng, C.L. Lee, K. Hendrata, P.N. Yuh Yek, N. L. Ma, S.S. Lam, Production of value-added liquid fuel via microwave co-pyrolysis of used frying oil and plastic waste, Energy 162 (2018) 309–317, https://doi.org/10.1016/j.energy.2018.08.002.

[26] S.S. Lam, W.A. Wan Mahari, Y.S. Ok, W. Peng, C.T. Chong, N.L. Ma, H.A. Chase, Z. Liew, S. Yusup, E.E. Kwon, D.C.W. Tsang, Microwave vacuum pyrolysis of waste plastic and used cooking oil for simultaneous waste reduction and sustainable energy conversion: Recovery of cleaner liquid fuel and techno-economic analysis, Renew. Sustain. Energy Rev. 115 (2019) 109359, https://doi.org/10.1016/j.rser.2019.109359.

[27] W.A. Wan Mahari, C.T. Chong, W.H. Lam, T.N.S.T. Anuar, N.L. Ma, M.D. Ibrahim, S.S. Lam, Microwave co-pyrolysis of waste polyolefins and waste cooking oil: Influence of N2 atmosphere versus vacuum environment, Energy Convers. Manag. 171 (2018) 1292–1301, https://doi.org/10.1016/j.enconman.2018.06.073.

[28] A. J. Ragauskas et al., "Lignin valorization: Improving lignin processing in the biorefinery," *Science (80-.).*, vol. 344, no. 6185, 2014, doi: 10.1126/science.1246843.

[29] R.A. Sheldon, Green chemistry, catalysis and valorization of waste biomass, J. Mol. Catal. A Chem. 422 (2016) 3–12, https://doi.org/10.1016/j.molcata.2016.01.013.

[30] S. Ge, Y. Wu, W. Peng, C. Xia, C. Mei, L. Cai, S.Q. Shi, C. Sonne, S.S. Lam, Y. F. Tsang, High-pressure CO2 hydrothermal pretreatment of peanut shells for enzymatic hydrolysis conversion into glucose, Chem. Eng. J. 385 (2020) 123949, https://doi.org/10.1016/j.cej.2019.123949.

[31] A.G. Gayubo, B. Valle, A.T. Aguayo, M. Olazar, J. Bilbao, Pyrolytic lignin removal for the valorization of biomass pyrolysis crude bio-oil by catalytic transformation, J. Chem. Technol. Biotechnol. 85 (1) (2010) 132–144, https://doi.org/10.1002/jctb.v85:110.1002/jctb.2289.

[32] S. Czernik, A.V. Bridgwater, Overview of applications of biomass fast pyrolysis oil, Energy and Fuels 18 (2) (2004) 590–598, https://doi.org/10.1021/ef034067u.

[33] Q. Lu, X.L. Yang, X.F. Zhu, Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk, J. Anal. Appl. Pyrolysis 82 (2) (Jul. 2008) 191–198, https://doi.org/10.1016/j.jaap.2008.03.003.

[34] R.N. Hilten, K.C. Das, Comparison of three accelerated aging procedures to assess bio-oil stability, Fuel 89 (10) (2010) 2741–2749, https://doi.org/10.1016/j.fuel.2010.03.033.

[35] H. Sui, H. Yang, J. Shao, X. Wang, Y. Li, H. Chen, Fractional condensation of multicomponent vapors from pyrolysis of cotton stalk, Energy and Fuels 28 (8) (2014) 5095–5102, https://doi.org/10.1021/ef5006012.

[36] D. Fu, S. Farag, J. Chaouki, P.G. Jessop, Extraction of phenols from lignin microwave-pyrolysis oil using a switchable hydrophilicity solvent, Bioresour. Technol. 154 (2014) 101–108, https://doi.org/10.1016/j.biortech.2013.11.091.

[37] F. Stankovikj, A. G. McDonald, G. L. Helms, and M. Garcia-Perez, *Quantification of Bio-Oil Functional Groups and Evidences of the Presence of Pyrolytic Humins*, vol. 30, no. 8. 2016.

[38] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Characterization of bio-oils in chemical families, Biomass and Bioenergy 31 (4) (2007) 222–242, https://doi.org/10.1016/j.biombioe.2006.02.006.

[39] J. Lehto, A. Oasmaa, Y. Solantausta, and D. Chiaramonti, "Fuel oil quality and combustion of fast pyrolysis bio-oils Bioliquids-CHP View project ELETTRA View project," no. June, 2018, doi: 10.13140/RG.2.2.15925.99042.

[40] A. Oasmaa, T. Sundqvist, E. Kuoppala, M. Garcia-Perez, Y. Solantausta, C. Lindfors, V. Paasikallio, Controlling the phase stability of biomass fast pyrolysis bio-oils, Energy and Fuels 29 (7) (2015) 4373–4381, https://doi.org/10.1021/acs.energyfuels.5b00607.

[41] F. Stankovikj, A. G. McDonald, G. L. Helms, M. V. Olarte, and M. Garcia-Perez, *Characterization of the Water-Soluble Fraction of Woody Biomass Pyrolysis Oils*, vol. 31, no. 2. 2017.

[42] F. Stankovikj, M. Garcia-Perez, TG-FTIR Method for the Characterization of Bio-oils in Chemical Families, Energy and Fuels 31 (2) (2017) 1689–1701, https://doi.org/10.1021/acs.energyfuels.6b03132.s001.

[43] E.H. Lee, R.-s. Park, H. Kim, S.H. Park, S.-C. Jung, J.-K. Jeon, S.C. Kim, Y.-K. Park, Hydrodeoxygenation of guaiacol over Pt loaded zeolitic materials, J. Ind. Eng. Chem. 37 (2016) 18–21, https://doi.org/10.1016/j.jiec.2016.03.019.

[44] B. Yoosuk, J. Boonpo, P. Udomsap, S. Sukkasi, Investigation of operating parameters of water extraction processes for improving bio-oil quality, Korean J. Chem. Eng. 31 (12) (2014) 2229–2236, https://doi.org/10.1007/s11814-014-0190-4.

[45] R. Soysa, Y.S. Choi, S.K. Choi, S.J. Kim, S.Y. Han, Synergetic effect of biomass mixture on pyrolysis kinetics and biocrude-oil characteristics, Korean J. Chem. Eng. 33 (2) (2016) 603–609, https://doi.org/10.1007/s11814-015-0194-8.

[46] M. Staš, M. Auersvald, L. Kejla, D. Vrtiška, J. Kroufek, D. Kubička, Quantitative analysis of pyrolysis bio-oils: A review, TrAC - Trends Anal. Chem. 126 (2020) 2020, https://doi.org/10.1016/j.trac.2020.115857.

[47] C.M. Michailof, K.G. Kalogiannis, T. Sfetsas, D.T. Patiaka, A.A. Lappas, Advanced analytical techniques for bio-oil characterization, Wiley Interdisc. Rev. Energy Environ. 5 (6) (2016) 614–639, https://doi.org/10.1002/wene.208.

[48] Y. Wang, S. Wang, F. Leng, J. Chen, L. Zhu, Z. Luo, Separation and characterization of pyrolytic lignins from the heavy fraction of bio-oil by molecular distillation, Sep. Purif. Technol. 152 (Aug. 2015) 123–132, https://doi.org/10.1016/j.seppur.2015.08.011.

[49] X. Li, S.R.A. Kersten, B. Schuur, Extraction of acetic acid, glycolaldehyde and acetol from aqueous solutions mimicking pyrolysis oil cuts using ionic liquids, Sep. Purif. Technol. 175 (2017) 498–505, https://doi.org/10.1016/j.seppur.2016.10.023.

[50] J. Montoya, B. Pecha, F.C. Janna, M. Garcia-Perez, Micro-explosion of liquid intermediates during the fast pyrolysis of sucrose and organosolv lignin, J. Anal. Appl. Pyrolysis 122 (2016) 106–121, https://doi.org/10.1016/j.jaap.2016.10.010.

[51] R.J.M. Westerhof, N.J.M. Kuipers, S.R.A. Kersten, W.P.M. Van Swaaij, Controlling the water content of biomass fast pyrolysis oil, Ind. Eng. Chem. Res. 46 (26) (2007) 9238–9247, https://doi.org/10.1021/ie070684k.

[52] S. Zhang, X. Yang, H. Zhang, C. Chu, K. Zheng, M. Ju, L.e. Liu, Liquefaction of biomass and upgrading of bio-oil: A review, Molecules 24 (12) (2019) 2250, https://doi.org/10.3390/molecules24122250.

[53] G. Charis, G. Danha, E. Muzenda, and T. Nhubu, "Modeling a Sustainable, Self-Energized Pine Dust Pyrolysis System With Staged Condensation for Optimal Recovery of Bio-Oil," *Front. Energy Res.*, vol. 8, no. February, pp. 1–12, 2021, doi: 10.3389/fenrg.2020.594073.

[54] A.-C. Johansson, K. Iisa, L. Sandström, H. Ben, H. Pilath, S. Deutch, H. Wiinikka, O. G.W. Öhrman, Fractional condensation of pyrolysis vapors produced from Nordic feedstocks in cyclone pyrolysis, J. Anal. Appl. Pyrolysis 123 (2017) 244–254, https://doi.org/10.1016/j.jaap.2016.11.020.

[55] K. Owen, O. Fasina, S. Taylor, S. Adhikari, Thermal decomposition behavior of loblolly pine stemwood, bark, and limbs/foliage using TGA and DSC techniques, Trans. ASABE 58 (2) (2015) 509–518, https://doi.org/10.13031/trans.58.10787.

[56] Q. Zhao, M. Mäkinen, A. Haapala, J. Jänis, Thermochemical conversion of birch bark by temperature-programmed slow pyrolysis with fractional condensation, J. Anal. Appl. Pyrolysis 150 (2020) 104843, https://doi.org/10.1016/j.jaap.2020.104843.

[57] K.H. Kim, R.C. Brown, X. Bai, Partial oxidative pyrolysis of acid infused red oak using a fluidized bed reactor to produce sugar rich bio-oil, Fuel 130 (2014) 135–141, https://doi.org/10.1016/j.fuel.2014.04.044.

[58] G. Charis, G. Danha, and E. Muzenda, "Optimizing yield and quality of bio-oil: A comparative study of Acacia tortilis and pine dust," *Processes*, vol. 8, no. 5, 2020, doi: 10.3390/PR8050551.

[59] B.J. Álvarez-Chávez, S. Godbout, É. Le Roux, J.H. Palacios, V. Raghavan, Bio-oil yield and quality enhancement through fast pyrolysis and fractional condensation concepts, Biofuel Res. J. 6 (4) (2019) 1054–1064, https://doi.org/10.18331/BRJ2019.6.4.2.

[60] A. Moutsoglou, B. Lawburgh, J. Lawburgh, Fractional condensation and aging of pyrolysis oil from softwood and organosolv lignin, J. Anal. Appl. Pyrolysis 135 (2018) 350–360, https://doi.org/10.1016/j.jaap.2018.08.016.

[61] S. Ma, L. Zhang, L. Zhu, X. Zhu, Preparation of multipurpose bio-oil from rice husk by pyrolysis and fractional condensation, J. Anal. Appl. Pyrolysis 131 (2018) 113–119, https://doi.org/10.1016/j.jaap.2018.02.017.

[62] C. Wang, Z. Luo, R. Diao, and X. Zhu, "Study on the effect of condensing temperature of walnut shells pyrolysis vapors on the composition and properties of bio-oil," *Bioresour. Technol.*, vol. 285, no. March, p. 121370, 2019, doi: 10.1016/j.biortech.2019.121370.

[63] X.S. Zhang, G.X. Yang, H. Jiang, W.J. Liu, H.S. Ding, Mass production of chemicals from biomass-derived oil by directly atmospheric distillation coupled with co-pyrolysis, Sci. Rep. 3 (2013) 1–7, https://doi.org/10.1038/srep01120.

[64] X. Guo, S. Wang, Z. Guo, Q. Liu, Z. Luo, K. Cen, Pyrolysis characteristics of bio-oil fractions separated by molecular distillation, Appl. Energy 87 (9) (2010) 2892–2898, https://doi.org/10.1016/j.apenergy.2009.10.004.

[65] S. Wang, Y. Gu, Q. Liu, Y. Yao, Z. Guo, Z. Luo, K. Cen, Separation of bio-oil by molecular distillation, Fuel Process. Technol. 90 (5) (2009) 738–745, https://doi.org/10.1016/j.fuproc.2009.02.005.

[66] S. Rahman, R. Helleur, S. MacQuarrie, S. Papari, and K. Hawboldt, "Upgrading and isolation of low molecular weight compounds from bark and softwood bio-oils through vacuum distillation," *Sep. Purif. Technol.*, vol. 194, no. November 2017, pp. 123–129, 2018, doi: 10.1016/j.seppur.2017.11.033.

[67] C. del Pozo, J. Bartrolí, N. Puy, E. Fàbregas, Separation of value-added chemical groups from bio-oil of olive mill waste, Ind. Crops Prod. 125 (July) (2018) 160–167, https://doi.org/10.1016/j.indcrop.2018.08.062.

[68] P.K. Kanaujia, D.V. Naik, D. Tripathi, R. Singh, M.K. Poddar, L.N.S.K. Konathala, Y. K. Sharma, Pyrolysis of Jatropha Curcas seed cake followed by optimization of liquid-liquid extraction procedure for the obtained bio-oil, J. Anal. Appl. Pyrolysis 118 (2016) 202–224, https://doi.org/10.1016/j.jaap.2016.02.005.

[69] D.S. Fardyanti, M. -, H. Istanto, M.K. Anajib, P. -, U. Habibah, Extraction of phenol from bio-oil produced by pyrolysis of coconut shell, J. Phys. Sci. 29 (Supp. 2) (2018) 195–202, https://doi.org/10.21315/jps10.21315/jps2018.29.s210.21315/jps2018.29.s2.15.

[70] M. Garca-Pèrez, A. Chaala, C. Roy, Co-pyrolysis of sugarcane bagasse with petroleum residue. Part II. Product yields and properties, Fuel 81 (7) (2002) 893–907, https://doi.org/10.1016/S0016-2361(01)00215-0.

[71] C.R. Vitasari, G.W. Meindersma, A.B. de Haan, Water extraction of pyrolysis oil: The first step for the recovery of renewable chemicals, Bioresour. Technol. 102 (14) (2011) 7204–7210, https://doi.org/10.1016/j.biortech.2011.04.079.

[72] L.-E. Park, S. Ren, S. Yiacoumi, X.P. Ye, A.P. Borole, C. Tsouris, Separation of Switchgrass Bio-Oil by Water/Organic Solvent Addition and pH Adjustment, Energy and Fuels 30 (3) (2016) 2164–2173, https://doi.org/10.1021/acs.energyfuels.5b0253710.1021/acs.energyfuels.5b02537.s001.

[73] A.S.B.Z.Z. Abdulkhani, Characterization of Fast Pyrolysis Bio-Oil from Hardwood and Softwood Lignin, Energies (2020) 1–14.

[74] X. Hu, D. Mourant, R. Gunawan, L. Wu, Y.i. Wang, C. Lievens, C.-Z. Li, Production of value-added chemicals from bio-oil via acid catalysis coupled with liquid-liquid extraction, RSC Adv. 2 (25) (2012) 9366, https://doi.org/10.1039/c2ra21597g.

[75] S. Ren, X.P. Ye, A.P. Borole, Separation of chemical groups from bio-oil water-extract via sequential organic solvent extraction, J. Anal. Appl. Pyrolysis 123 (2016) (2017) 30–39, https://doi.org/10.1016/j.jaap.2017.01.004.

[76] S. Wang, Y. Wang, Q. Cai, X. Wang, H. Jin, Z. Luo, Multi-step separation of monophenols and pyrolytic lignins from the water-insoluble phase of bio-oil, Sep. Purif. Technol. 122 (2014) 248–255, https://doi.org/10.1016/j.seppur.2013.11.017.

[77] "Pyrolysis of wood biomass for bio-oil a critical review.pdf." .

[78] P. Das, T. Sreelatha, A. Ganesh, Bio oil from pyrolysis of cashew nut shell-characterisation and related properties, Biomass and Bioenergy 27 (3) (2004) 265–275, https://doi.org/10.1016/j.biombioe.2003.12.001.

[79] V.T.T. Energy, Characterization of biomass-based flash pyrolysis oils, Fuel Energy Abstr. 40 (1) (1999) 15–16, https://doi.org/10.1016/s0140-6701(99)92423-2.

[80] Z. Shah, R. CV, M. AC, and R. DS, "Separation of Phenol from Bio-oil Produced from Pyrolysis of Agricultural Wastes," *Mod. Chem. Appl.*, vol. 05, no. 01, pp. 1–8, 2017, doi: 10.4172/2329-6798.1000199.

[81] X. Yang, H. Lyu, K. Chen, X. Zhu, S. Zhang, J. Chen, Selective Extraction of Bio-oil from Hydrothermal Liquefaction of Salix psammophila by Organic Solvents with Different Polarities through Multistep Extraction Separation, BioResources 9 (3) (2014) 5219–5233, https://doi.org/10.15376/biores.9.3.5219-5233.

[82] L. Zhang, R. Liu, R. Yin, Y. Mei, Upgrading of bio-oil from biomass fast pyrolysis in China: A review, Renew. Sustain. Energy Rev. 24 (2013) 66–72, https://doi.org/10.1016/j.rser.2013.03.027.

[83] B. William, P. Noémie, E. Brigitte, P. Géraldine, Supercritical fluid methods: An alternative to conventional methods to prepare liposomes, Chem. Eng. J. 383 (August) (2020) 2020, https://doi.org/10.1016/j.cej.2019.123106.

[84] T. Cheng, Y. Han, Y. Zhang, C. Xu, Molecular composition of oxygenated compounds in fast pyrolysis bio-oil and its supercritical fluid extracts, Fuel 172 (2016) 49–57, https://doi.org/10.1016/j.fuel.2015.12.075.

[85] Y. Feng, D. Meier, Comparison of supercritical CO2, liquid CO2, and solvent extraction of chemicals from a commercial slow pyrolysis liquid of beech wood, Biomass and Bioenergy 85 (2016) 346–354, https://doi.org/10.1016/j.biombioe.2015.12.027.

[86] F. Zeng, W. Liu, H. Jiang, H.Q. Yu, R.J. Zeng, Q. Guo, Separation of phthalate esters from bio-oil derived from rice husk by a basification-acidification process and column chromatography, Bioresour. Technol. 102 (2) (2011) 1982–1987, https://doi.org/10.1016/j.biortech.2010.09.024.

[87] H.-M. Yang, W. Zhao, K. Norinaga, J.-J. Fang, Y.-G. Wang, Z.-M. Zong, X.-Y. Wei, Separation of phenols and ketones from bio-oil produced from ethanolysis of wheat stalk, Sep. Purif. Technol. 152 (2015) 238–245, https://doi.org/10.1016/j.seppur.2015.03.032.

[88] S.J. Andersen, T. Hennebel, S. Gildemyn, M. Coma, J. Desloover, J. Berton, J. Tsukamoto, C. Stevens, K. Rabaey, Electrolytic membrane extraction enables production of fine chemicals from biorefinery sidestreams, Environ. Sci. Technol. 48 (12) (2014) 7135–7142, https://doi.org/10.1021/es500483w.

[89] A.P. Pinheiro Pires, J. Arauzo, I. Fonts, M.E. Domine, A. Fernández Arroyo, M. E. Garcia-Perez, J. Montoya, F. Chejne, P. Pfromm, M. Garcia-Perez, Challenges

and opportunities for bio-oil refining: A review, Energy and Fuels 33 (6) (2019) 4683–4720, https://doi.org/10.1021/acs.energyfuels.9b00039.

[90] J.S. Kim, Production, separation and applications of phenolic-rich bio-oil - A review, Bioresour. Technol. 178 (2015) 90–98, https://doi.org/10.1016/j.biortech.2014.08.121.

[91] S. Hansen, A. Mirkouei, and L. A. Diaz, "A comprehensive state-of-technology review for upgrading bio-oil to renewable or blended hydrocarbon fuels," *Renew. Sustain. Energy Rev.*, vol. 118, no. October 2019, p. 109548, 2020, doi: 10.1016/j.rser.2019.109548.

[92] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of two bio-oil upgrading pathways, Chem. Eng. J. 225 (2013) 895–904, https://doi.org/10.1016/j.cej.2013.01.030.

[93] Y. Sorunmu, P. Billen, S. Spatari, A review of thermochemical upgrading of pyrolysis bio-oil: Techno-economic analysis, life cycle assessment, and technology readiness, GCB Bioenergy 12 (1) (2020) 4–18, https://doi.org/10.1111/gcbb.v12.110.1111/gcbb.12658.

[94] J.L. Zheng, Y.H. Zhu, M.Q. Zhu, G.T. Sun, R.C. Sun, Life-cycle assessment and techno-economic analysis of the utilization of bio-oil components for the production of three chemicals, Green Chem. 20 (14) (2018) 3287–3301, https://doi.org/10.1039/c8gc01181h.

[95] W. Maqbool, K. Dunn, W. Doherty, N. McKenzie, D. Cronin, P. Hobson, Extraction and Purification of Renewable Chemicals from Hydrothermal Liquefaction Bio-oil Using Supercritical Carbon Dioxide: A Techno-economic Evaluation, Ind. Eng. Chem. Res. 58 (13) (2019) 5202–5214, https://doi.org/10.1021/acs.iecr.8b0536610.1021/acs.iecr.8b05366.s001.

[96] B. Valle, A. Remiro, N. García-Gómez, A. G. Gayubo, and J. Bilbao, "Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: a review," *Journal of Chemical Technology and Biotechnology*, vol. 94, no. 3. John Wiley and Sons Ltd, pp. 670–689, Mar. 01, 2019, doi: 10.1002/jctb.5758.

[97] X. Hu and M. Gholizadeh, "Progress of the applications of bio-oil," *Renew. Sustain. Energy Rev.*, vol. 134, no. December 2019, p. 110124, 2020, doi: 10.1016/j.rser.2020.110124.