



An overview of recent development in bio-oil upgrading and separation techniques

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ABSTRACT

Bio-oil produced from the fast pyrolysis/hydrothermal liquefaction is gaining popularity worldwide as the forerunner to replace fossil fuel. The bio-oil can be produced from agricultural waste, forest residue, and urban organic waste. It is also called pyrolysis oil, renewable fuel, and has the potential to be used as fuel in many applications. The application of bio-oil as transportation fuel helps to reduce the emission of greenhouse gases and to keep up the ecological balance. The bio-oil has the heating value of nearly half of the diesel fuel i.e. 16-19 MJ/kg; but, the inferior properties such as high water content, high viscosity, low pH, and poor stability hinder bio-oil application as a fuel. Thus, this paper provides a detailed review of bio-oil properties, its limitations and focuses on the recent development of different upgrading and separation techniques, used to date for the improvement of the bio-oil quality. Furthermore, the advantages and disadvantages of each upgrading method along with the application and environmental impact of bio-oil are also discussed in this article.

Keywords: Bio-oil, Environmental impact, Fast Pyrolysis, Separation, Upgradation

1. Introduction

The world energy demand is increasing at an exponential rate with the cause of an increasing trend of population. The present energy consumption pattern is showing a significant effect on the global economy as well as on the environment. The major sources of energy include fossil fuel such as natural gas, coal, and petroleum. The current consumption of petroleum and other liquid fuel is 100.72 million barrels per day [1]. However, renewable fuels are gaining much attention to replace conventional fuel and to fill the energy gap. Biofuel is one of the promising options of renewable energy gaining popularity globally, as it can produce fuel with similar functionality of crude oil [2]. Biofuels are produced from biomass by either thermochemical or biochemical conversion routes. The biochemical conversion route involves mainly anaerobic digestion and fermentation. The organic waste or biomass is subjected to degrade by means of micro-organism or bacteria to produce liquid and gaseous fuel. The biofuels such as biogas and ethanol are the products of the anaerobic digestion and fermentation, respectively. The biogas is a gaseous fuel formed by the decomposition of organic waste in anaerobic conditions. However, ethanol is a liquid fuel

formed by the fermentation of feedstock with the help of yeast. Both anaerobic digestion and fermentation are commercially successful and used at large scale to produce biofuel [3].

The thermochemical conversion includes combustion, gasification, pyrolysis, and hydrothermal liquefaction. Among thermochemical conversion techniques, pyrolysis is the process used to provide solid, gas, and liquid type of fuels, as per the need. Pyrolysis oil or Bio-oil produced from the pyrolysis of biomass has been identified as potential fuel to replace fossil fuel in many applications, if produced and processed properly [4, 5].

The fast pyrolysis process in which the cellulose, hemicellulose, and lignin of biomass are decomposed into mainly liquid (60-75 wt%), solid (15-25 wt%), and gases (12-15 wt%) products when heated at a temperature about 450 to 600°C [6, 7]. Bio-oil can be made from different feedstocks such as wood, agricultural waste, forest residues, and municipal solid waste. The yield and chemical composition of bio-oil depend upon the percentage of cellulose, hemicellulose, and lignin present in the biomass. This composition of biomass has different thermal behavior and it is strongly dependent on the heating rate used in the pyrolysis process [4]. However, Demirbas and Arin [8] reported that during the pyrolysis of biomass,



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Table 1. Lignocellulose Percentage in Biomass

Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Wheat straw	29-35	26-32	16-21	[10]
Corn cobs	45	35	15	[11]
Corn Stover	38	26	19	[12]
Sweet sorghum	45	27	21	[13]
Sugarcane bagasse	42	25	20	[13]
Rice straw	32	24	18	[11]

hemicellulose is the first to start to degrade at a temperature from 200 to 260°C and cellulose starts to degrade at a temperature from 240 to 350°C and lignin is the last component to degrade from 280 to 500°C. Cellulose is a major component of biomass which could be converted into bio-oil and hemicellulose and lignin converted partially into oil and gas at a pyrolysis temperature of 450 to 600°C [9]. Table 1. shows the percentage of cellulose, hemicellulose, and lignin available in different biomass.

Presently, fast pyrolysis and hydro-thermal liquefaction are the two most used techniques for bio-oil productions. From the last two decades, fast pyrolysis for bio-oil production has been receiving wide attention as it is the simplest and economical way to convert biomass into liquid fuel. The fast pyrolysis of biomass required the following conditions, the higher heating rate for rapid thermal decomposition of biomass i.e. > 100°C/min [14], size of biomass < 1 mm, and controlled temperature of 500°C [15]. Extensive research has been carried to enhance the quality and quantity of bio-oil to date by developing several pyrolysis reactors such as fluidized bed, circulating fluidized bed, fixed bed, ablative reactor, auger, and vacuum reactor [16, 17]. However, these types of reactors have advantages and limitations compare to each other [18]. Rasul and Jahiril [19] reported that the fluidized bed technology is the most suitable technology for the production of optimum bio-oil, due to the high heating rate during the process, easy to operate and trouble-free char collection.

Hydrothermal liquefaction (HTL) is a new and developing process of bio-oil production. The breakdown of the biomass was carried out at high temperatures and pressure under the presence of water. The temperature and pressure required in the HTL process are in the range of 250°C to 374°C and 4 to 22MPa [20]. The quality of bio-oil produced from HTL is better than fast pyrolysis because it has lower oxygen content and higher heating value than the produced bio-oil from fast pyrolysis [21, 22]. Due to the high requirement of pressure make HTL, an uneconomical process and hinders its scale up and commercialization. Moreover, in this paper properties of bio-oil produced from fast pyrolysis are only discussed in detail. Bio-oil is a complex mixture of water, solid particles, and contains several hundreds of organic compounds [23]. The bio-oil has ten times more density than the raw or loose biomass, it is easy to transport and can be used as an efficient energy carrier [24]. Bio-oil having a higher heating value between 16-19 MJ/kg [25], which is approximately 40% of the heating value of diesel fuel. Despite the above advantages, bio-oil has limitations such as high water content, high viscosity, and low heating value [7]. The presence of organic acids causes corrosion to common materials as well as aldehydes and large molecular oligomers make it difficult

to use bio-oil as transport fuel [26, 27].

Therefore, to replace partially or fully transportation fuel by bio-oil, it is obligatory to improve the quality of bio-oil by upgrading. So far, extensive study has been carried out on the different types of reactors used in fast pyrolysis, factors affecting bio-oil production and application of bio-oil. It is evident that the bio-oil contains several hundred compounds, but few of them are available in a significant amount and have a commercial value such as acetic acid, acetol, glycolaldehyde, and levoglucosan. The other compounds, which also has commercial value but available in very low fractions are phenol, pyrolytic lignin, ketones, and oligomers [28]. Accordingly, more research is required for the separation and upgrading techniques of bio-oil. This review focuses on the recent development in the improvement of bio-oil quality by using different upgradation and separation techniques to recover different chemicals from bio-oil. As well as the properties, environmental impact, and suitable application of bio-oil are also discussed.

2. Properties of Bio-Oil

Bio-oil is a dark brown liquid produced from fast pyrolysis of agricultural residues. The fresh produced bio-oil is free flowing in nature, containing 15-35% water. The color of the bio-oil changes from dark brown to red-brown owing to the removal of solid particles or char. The bio-oil shows the similar proximate and ultimate characteristics to the biomass from which it is produced. However, based on the pyrolysis conditions such as temperature, residence time, and type of carrier gas used, the properties of the bio-oil may vary.

Table 2. Properties of Bio-Oil [32]

Properties	Typical Bio-oil	Crude oil
Water content (wt.%)	10-30	0.1
pH	2.8-3.8	-
	C	55-65
	H	5-7
	O	11-14
Elemental composition (wt.%)	28-60	< 1.0
	N	< 0.4
	S	< 0.05
	< 4	< 4
Solid (wt.%)	< 0.2	0.1
HHV (MJ/kg)	16-19	44
H/C	0.9-1.5	1.5-2.0
O/C		0.3-0.5
Viscosity (at 50°C, cP)	40-100	180

Apparently, bio-oil is a mixture of oily phase and aqueous phase [29], and it is characterized based on the following physicochemical properties like water content, oxygen content, density, heating value, acid value, viscosity, and ash content. These properties are the indicators of the bio-oil potential to be used fuel, in the range of petrol and diesel. The properties of typical bio-oil and crude oil are shown in Table 2. Apart from the physical properties shown in Table 2, the following chemical compounds are identified in bio-oil such as acids, alcohols, aldehydes, ketones, phenols, sugar, ester, furans, guaiacols, and multifunctional components [20, 30, 31].

2.1. Water Content

The percentage of water in bio-oil varies from 15-35% depending upon the type of feedstock and pyrolysis condition [33]. The water in bio-oil is come from the original water content in biomass and during the pyrolysis reaction of biomass such as dehydration and de-polymerization. However, the water in bio-oil possesses advantages and disadvantages such as lowering the viscosity to make it free-flowing liquid and also lowers the heating value and flame temperature, resulted in ignition difficulties, respectively. The bio-oil with high water content can be used in engines or boilers but it requires some modification and circumstances [34]. As regulated in bio-oil norms and standard ASTM D 7544 fast pyrolysis oil (Grade D and G), the maximum permissible water content is 25-30% to use as fuel in the turbine and boiler [35]. Due to the effect of solubilizing compounds present in the bio-oil such as acids, alcohols, ketone and aldehydes make it difficult to separate water from bio-oil [36]. Generally, the Karl Fischer titration method is used to determine the water content by following ASTM E 203 [37].

2.2. Oxygen Content

The high content of oxygen in bio-oil is due to the presence of

high water in bio-oil. Moreover, bio-oil contains hundreds of oxygenated compounds that make bio-oil polar as well as non-miscible with petroleum fuel [23], and these compounds contributed 40-50 wt.% of the oxygen content in bio-oil [38]. The high oxygen content in bio-oil makes bio-oil significantly differ from conventional fuels, it reduces heating value and unstable during storage and transportation. The oxygen content of bio-oil is determined by elemental analysis of C, H, N, and S in percent of weight, and remaining is considered as oxygen.

2.3. Density and Viscosity

The density of bio-oil is a crucial property when it is to be used as fuel in engines. The bio-oil density is found in the range of 1,000-1,200 kg/m³, it may differ on the basis of the type of feedstock and pyrolysis conditions. However, the density of (petroleum fuel) diesel is found in the range of 840 to 860 kg/m³ [39]. If bio-oil is directly used as fuel in an engine, due to the higher density, it poses a difficulty for fuel injectors and leads to the emission of heavy pollutants.

The viscosity is defined as a measure of the resistance of a fluid to flow. The viscosity of bio-oil is directly linked with its water content. The viscosity of bio-oil produced from different feedstock varied in the range of 35-1,000 cP at 40°C [4]. The higher the water content of bio-oil, the higher the viscosity, however at room temperature the viscosity decreases and also changes with time and temperature during storage [25]. Moreover, the addition of a polar solvent such as methanol, ethanol, and acetone helps to decrease the viscosity of bio-oil [38, 40]. The viscosity of bio-oil not only depends upon the type of feedstock, processing condition but also on the collection procedure of bio-oil.

2.4. Acidity

The presence of organic acids such as carboxylic acid, acetic acid,

Table 3. Cause and Limitations of Bio-Oil Characteristics [46]

Sr. No	Bio-oil characteristics	Limitations/problem	Cause
1.	High viscosity	Phase separation	High ash in feed, high water content in bio-oil, and increase in molecular mass of liquid.
2.	High water content	Seriously affects the viscosity and stability of bio-oil, lowers heating value	Pyrolysis reaction and initial water present in feed
3.	Low heating value	Low grade fuel	Due to increase in water content and high oxygen content
4.	Acidity	Corrosion of system parts and pipelines	Degradation of organic acid present in feed
5.	Low H:C ratio	Low grade fuel	H:C ratio of feed is low
6.	Poor distillability	Difficult to upgrade, because bio-oil begins to react at below 100°C	Reactive mixture of degradation product of feed
7.	Non-miscibility with hydrocarbon fuel	Difficult to mix with hydrocarbon fuel, hence remain low grade fuel	Presence of oxygenated nature of bio-oil
8.	Aging	Increase in viscosity, cannot store in open air, for long time	Secondary reactions including polymerization
9.	Smell	The smell is often objectionable (not toxic)	Presence of hemicellulose to form aldehyde and other volatile organics
10.	Solid/char	Aging of bio-oil, sedimentation, erosion, and blockage of line	Inefficient separation of char or other solid contaminants.

and formic acid makes bio-oil acidic i.e. found pH in the range of 2 to 3. The low pH value makes bio-oil corrosive to some material such as carbon steel, copper, iron, and aluminum which mainly impede the bio-oil application as an engine fuel. The ASTM D664 test method was used to measure the total acid number (TAN) of bio-oil to evaluate the acidity [41].

2.5. Ash Content

The presence of ash and char in the bio-oil makes it difficult to use bio-oil as fuel. The ash percentage in bio-oil found in the range of 0.01 to 0.5% [42]. The ash constitutes mainly alkali metals such as potassium and sodium which are catalytically active and promotes the secondary cracking of vapors. It results in loss of liquid yield and higher water content in bio-oil [4]. The ash in bio-oil produces inevitable problems such as poor combustion, erosion, corrosion of metals, and blockage of engine parts [43].

2.6. Aging (Instability)

The fresh bio-oil contains reactive compounds in it, which were formed during the thermal decomposition of biomass and rapid quenching of vapors. These compounds are the major cause to change in the physical and chemical properties of bio-oil during storage and transportation [44]. The active organic functional groups found in bio-oil are aldehydes, carboxylic acid, alcohols, phenol, and unsaturated hydrocarbons, and their percentage is subjected to change during storage. Moreover, the polar solvent such as methanol used to improve the viscosity and homogeneity of the bio-oil [45]. The cause and limitations of bio-oil different characteristics are presented in Table 3.

3. Separation of Bio-Oil Compounds

The direct application of bio-oil as fuel is not possible because of its inferior properties, described earlier. Although, bio-oil contains several organic compounds, which can be upgraded to fuel or value-added chemicals [47]. The presence of acids such as acetic acid and formic acids are the main cause of the high acidity of bio-oil. Therefore, it is necessary to remove these acids, on the other hand, these acids have tremendous demand in the global market [48]. Moreover, the compounds such as guaiacol, anisole, phenol, phenolic monomers, furans, dimers, and carboxylic acids is can be further upgraded to obtain hydrocarbons using various upgrading methods or can be used as raw feedstock in the chemical industry. Therefore, the separation of bio-oil is found as an indispensable step before upgrading of bio-oil. The importance of separation technology in making bio-refinery a successful concept has been presented by Kiss et al. [49]. It is observed that the upgrading of specific compounds rather than the whole bio-oil is found effective and economical. However, the studies by Teella et al. [50]; Oh et al. [51] observed that the separation of chemicals from bio-oil is not a feasible process due to the low percentage recovery of chemicals and the high cost of the process. It has been observed that the combination of efficient bio-oil separation method and suitable upgrading methods is the need for the future to produce high graded bio-oil and value-added chemicals from biomass

at an economical rate. The conventional techniques used for bio-oil separation are solvent extraction, distillation, column chromatography.

3.1. Distillation

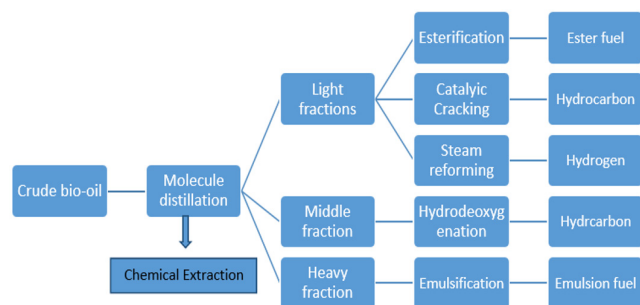
Distillation is the process used to separate components from a liquid mixture based on boiling point or volatility. The water content in bio-oil is the major cause of its low heating value, this water can be removed by the distillation process. Azeotropic distillation [52], atmospheric pressure distillation, steam distillation, and vacuum distillation have been used in bio-oil separation [53, 54]. Suota et al. [55] experimented on the crude bio-oil obtained from the fast pyrolysis of waste cooking oil. Then it distilled at boiling point of gasoline and diesel, which delivers light and heavy bio-oil fractions of 30 and 50%, respectively. The components of light of bio-oil are found comparable to gasoline while heavy bio-oil consists mainly, alkanes, alkenes and esters.

The bio-oil has a very complex composition, therefore the boiling of some component starts below 100°C under atmospheric pressure but only some compounds like acetic acid, furfural, and propanoic acid recovered with efficiency more than 80 % from bio-oil using atmospheric distillation [56]. Consequently, atmospheric distillation not showed a significant result. Besides, to separate bio-oil efficiently below 100°C, a vacuum distillation system is used, to lower the boiling point of several components and separate bio-oil at a lower temperature. Rahman et al. [48] reported that the residual bio-oil after vacuum distillation at 100°C and 10 kPa, contains 55-60% less water than the crude bio-oil, the heating value and acidity of bio-oil found improved. The study also revealed that distilled bio-oil contains low molecular weight compounds such as acetic acid, acetol, acrolein, methanol, and glycolaldehyde. The distilled organic fraction from bio-oil shows lower water content, less oxygenated compounds, and improved higher heating value than crude bio-oil. Choi et al. [57] reported that the vacuum distillation of bio-oil produced from *Saccharina japonica* under reduced pressure of 40 mmHg and at a temperature of 40 to 160°C gives the two phases of bio-oil i.e. heavy and light fractions. This may be due to the presence of different polarities of sugars and aromatics available in bio-oil. However, Murwanashyaka et al. [58] found that the combination of steam and pressure distillation recovered approximately 15% of volatile fractions. Furthermore, Nam et al. [59] compared the fractional distillation and vacuum distillation, concluded that vacuum distillation founds effective in terms of bio-oil quality than fractional distillation while maximum mass yield was obtained from fractional distillation. However, the different characteristics of distilled by bio-oil were compared to gasoline, shown in Table 4.

These conventional techniques of bio-oil separation have not been found efficient. Recently, more attention has been given on the molecular distillation, as it has some advantages such as it required low operating temperature, less heating time, and high efficiency [33, 60]. The light and weight fractions of bio-oil are separated by molecular distillation and the obtained light fraction can be used as the substance for the upgradation process [61]. A scheme of combining the process of molecular distillation and upgrading of bio-oil to form a high grade fuel is shown in Fig. 1.

Table 4. Comparison of Characteristics of Distilled Bio-Oil and Gasoline [59]

	Moisture content	Kinematic viscosity at 40°C (cSt)	HHV, (MJ/kg)	TAN (mg KOH/g)	pH
Crude bio-oil	8.20	3.52	38.6	12.0	8.7
Fractional distillation	2.17	0.60	40	0.12	9.9
Vacuum distillation	1.6	0.67	40.5	0.10	9.7
Gasoline	< 0.1	0.12-0.4 (@15°C)	43-47	-	-

**Fig. 1.** Combining process of molecule distillation and bio-oil upgrading, [154]

3.2. Solvent Extraction

A solvent extraction method was used to separate the bio-oil into different chemical groups based on the polarities of the available compound in bio-oil. A solvent such as water, ethyl acetate, ethers, ketones, and chloroform as well as toluene and n-hexane were used to separate the bio-oil [62-64]. The bio-oil separation using water fractionation gives water-soluble and water-insoluble fractions, further mixing of solvent in it, leads to the separation of compounds [65]. However, Wei et al. [64] reported that chloroform solvent can be used to extract phenol and guaiacols with 85% recovery efficiency. Similarly, a solvent such as diethyl ether and dichloromethane used to separate the acetic acid and phenolic compounds from the crude bio-oil [66, 67].

Del Pozo et al. [68] reported that an acid based extraction method performed with hexane extraction at pH 12 followed by an ethyl acetate extraction at pH 6 was found better in separating the value-added chemicals such as phenol, ketones, acetic acids, and carboxylic acids from the aqueous and non-aqueous phases of bio-oil. The acetic acid recovered from the bio-oil can be used to produce hydrogen as an energy source in the upgradation process of bio-oil i.e. hydrodeoxygenation.

However, due to the high amount of solvent requirement, which makes it economically unfeasible, not suitable for industrialization. Shah et al. [63] efficiently recovered phenol from bio-oil using solvent ethyl ether, caustic soda, and hydrochloric acid (HCl). Further, the obtained phenol can be used in the production of resins, dyes, lubricants, pesticides, plastic, and explosives. In recent times, supercritical fluid extraction has gained much attention, as it required low temperature due to which thermally sensitive components from bio-oil can be extracted [69]. Wang et al. [70] reported that supercritical CO₂ extraction methods involve high extraction pressure and relatively low temperature helps to reduce the water content of bio-oil. The study concludes that the calorific value and stability of bio-oil improved with reaching an extraction

efficiency of 88.6%.

3.3. Column Chromatography

The principle of column chromatography is that it separates the component from the mixture by adsorption. The bio-oil is allowed to pass through a column of solid stationary phase; generally, silica is used, under the force of the liquid mobile phase. An eluent i.e. carrier of the mobile phase is selected based on the polarity of components of bio-oil to be separated. Thus, bio-oil can be separated based on the polarity, type of solvents, and properties of adsorbents in column chromatography [71]. Generally, an eluent with a single solvent is used to separate aromatic, aliphatic, and some polar fractions. The eluents used in bio-oil separation are hexane, toluene, benzene, pentane, ethyl acetate, and methanol [72-74]. However, Hao et al. [75] reported that the valuable chemical compound like syringol and acetosyringone can be effectively separated from column chromatography.

4. Upgradation of Pyrolysis Oil

As discussed above the properties and limitations of bio-oil, the direct application of bio-oil as petroleum-based fuel is inconceivable. The limitations of bio-oil can be removed by different upgrading methods, however intensive research has been done so far on upgrading methods of bio-oil. Here, recent development in bio-oil upgradation methods is presented. Upgradation of bio-oil can be classified as the following three types, shown in Fig. 2.

4.1. Filtration (Hot Vapor Filtration)

The presence of char in the vapor as well as in liquid oil leads to poor quality and quantity of oil, reduction of viscosity and lowers the average molecular weight of the oil [7]. The Hot Vapor filtration (HVF) is used to upgrade the bio-oil physically by removing bio-char (including ash) and alkali content from crude bio-oil. The hot gas filter is used to filter the gas or vapor at a temperature above 260°C. The conventional filters like bag-type failed at higher temperatures due to its material of construction. Whereas the hot vapor filter consists of a filter element, a candle like structure, which receives the gases from one end and other end is closed. The filter media used in HVF is made up of ceramic or metal (stainless steel), porous sintered steel (pss) sintered metal powder, sintered ceramic powder, flexible ceramic cloth, rigid sintered, stainless steel, glass wool, and polycarbonate film [71, 76- 82].

Generally, the cyclone is used to capture the solid particles from the vapor, but it can only detain particles in the range of 10-170 μm size and the HVF catches particles less than size 0.3μm.

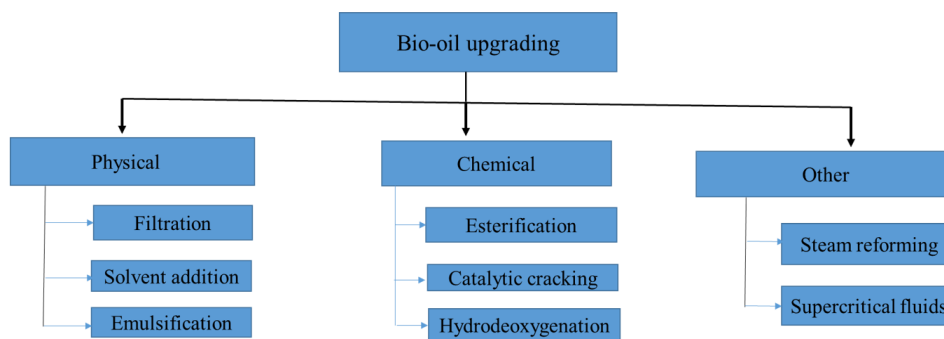


Fig. 2. Upgrading methods of bio-oil.

The study conducted by Wang [77] reported that five times less ash was found in the filtered bio-oil than non-filtered bio-oil. The type of filter media also has a profound effect on the properties of bio-oil. The ceramic type filtered found satisfactory because filtered oil gives less iron content, solid and alkali content, as well as the viscosity of the filtered bio-oil, were also found much increased than the non-filtered oil after the aging test [76, 78, 80, 81]. The temperature of HVF plays a major role in the quality and quantity of bio-oil. Mei et al. [83] reported that the maximum yield of organic liquid was obtained when the temperature of HVF reached from 350 to 400°C. It was reported that the removal of solid particles including alkali metals helps to increase the organic liquid content of bio-oil. The performance of filtered bio-oil tested in a diesel engine by Shihadeh [84], it was observed that the burning rate and ignition delay of filtered oil was better than crude bio-oil. The effect and limitations of HVF are presented in Table. 5.

4.2. Solvent Addition

The presence of highly active oxygen containing compounds and high viscosity hinders bio-oil application as a transport fuel (conventional fuel). The viscosity of bio-oil generally increases over time due to the condensation and polymerization of a water-insoluble fraction [66]. The addition of a solvent such as methanol, ethanol, ethyl acetate, and acetate to the bio-oil helps in homogenizing and to lower the viscosity and density as well as to increase the higher heating value of bio-oil [85]. The addition of alcohol helped to improve the homogeneity of the bio-oil by preventing the phase separation. The raw bio-oil having some soluble hydrophobic compounds by adding alcohol the solubility of those compounds increased and it leads to separate the extractive rich top layer from the bio-oil [86].

Oasmaa et al. [86] investigated the addition of methanol, ethanol, and isopropanol into bio-oil. Methanol founds most effective among the ethanol and isopropanol in terms of viscosity and stability of bio-oil. Whereas, ethanol addition increased the heating value of bio-oil as compared to methanol. The addition of methanol to the bio-oil not only reduces the viscosity by lowering the polymerization and aging reaction but it also uses to increase the acidity of bio-oil. Mei et al. [87] observed that the pH of bio-oil during storage was increased from 2.32 to 3.26 when methanol was added at 15 wt.%, after 35 day storage. More recently, Zhu et al. [88] studied the effect of the addition of a compound additive solvent such as methanol (1 wt.%), N- dimethylformamide (5.06 wt.%),

and acetone (1.94 wt.%) to the bio-oil. The result showed that the viscosity, water content, and pH of the bio-oil was better than the single solvent added bio-oil. The more about solvent upgrading method is also presented in Table. 5.

4.3. Emulsification

The Emulsion is the process of dispersion, made up of mixing two not miscible liquids with the help of mechanical shear (agitation) or with the help of surfactant [89]. The one phase of liquid such as droplets is dispersed into the other phase of liquids. The application of bio-oil directly with diesel is not adequate due to the content of polar compounds. The blending of bio-oil with diesel and the addition of surfactant is the best way to improve the bio-oil properties to be used as transport fuel [90-92]. Emulsification is an economic, easy, and simple method of upgradation of bio-oil [93, 94]. The choice of surfactant plays an important role in the process, and its selection depends on the hydrophilic-lipophilic balance (HLB) value and chemical properties of the surfactant. The HLB value of the surfactant is used to indicate the chemical properties and characteristics of the surfactant, generally, the HLB values range from 0-20 and characterized it into two groups, lipophilic (4-8) and hydrophilic group (9-15). The emulsification of bio-oil required the following condition to be satisfied [95].

1. Two immiscible liquids i.e. bio-oil and diesel
2. Additives, surfactant and co-surfactant
3. External energy source for agitation

The emulsification of bio-oil with diesel is not an easy process, because of the complexity of bio-oil. In the emulsification process of bio-oil in diesel, the dispersed bio-oil formed the water phase while diesel fuel formed a true oil phase [96]. For the effective emulsification of bio-oil with diesel, the percentage of bio-oil, diesel, and surfactant was found best in the range of 10-50%, 50-90%, and 1-10%, respectively [97, 98]. The emulsification process improves the heating value, pH, and stability of bio-oil [98]. However, the percentage bio-oil in the emulsification affects the viscosity of emulsion, higher the bio-oil content higher the viscosity of the emulsion, hence bio-oil and surfactant content of 10-20 wt.% and 4-6 wt.%, respectively were found optimal to produce a stable emulsified bio-oil [90, 92]. The addition of alcohol such as methanol, ethanol, and n-butanol as co-surfactants were found favorable in improving the stability of the bio-oil emulsion [99, 100]. Moreover, to improve the stability of emulsified bio-oil, the ether extracted bio-oil (EEO) was emulsified with diesel, Span 80 and Tween 60

were used as an emulsifier. The result showed that the heating value of emulsified EEO increased to 44 MJ/kg and the stability of emulsions remains for 40 days [101]. The emulsifiers play a very crucial role in the emulsification process. The following types of emulsifiers were used in the emulsification of bio-oil such as Span 60, Span 80, Span 85, Span 100, Tween 80, Lecithin, Atlox 4914, Lignin, PGO, Lanolin, Hypermer B246, Brij 58, and Brij 72 [29, 96-98, 102-104]. The two or more emulsifiers can also be blended to obtain the best HLB value for the effective emulsification process but sometimes the combination of two different emulsifiers is not a decent option due to the thermal stability differences [105]. Another application of emulsified bio-oil is lubrication and the lubrication ability of the emulsion is can be increased with increasing the critical content of bio-oil in emulsion [97].

4.4. Esterification

Esterification is the process of forming ester from the reaction of carboxylic acids with alcohol. Esters are more anticipated than acids in fuel and are less corrosive, suitable for engine application. The Bio-oils have high organic acids; it can be converted into corresponding esters by the addition of alcohol and some catalysts such as zeolite and resins [106-109]. The esterification process gives bio-oil with a lowered acid number, density, water content, and increased heating value [106, 107]. The process of esterification of bio-oil with ethanol or methanol is generally carried at a temperature of 55°C- 60°C and with the residence time of 1-4 hours [110]. The surplus advantage of adding alcohol in the bio-oil directly reduces the viscosity and increases the heating value of bio-oil. However, Milina et al. [111] suggested that catalytic esterification as an obliging step to upgrade bio-oil prior to hydrotreating because catalytic esterification reduces the acidity and oxygen content of the bio-oil. Moreover, the requirement of hydrogen in the further refining process would also get reduced due to catalytic esterification. The application of solid acid catalysts such as zeolite [111], aluminum silicate [112] ion exchange resin [106, 107], and an acid catalyst such as H₂SO₄, HCL, and citric acid [110] in the esterification process were also investigated. Whereas, Song et al. [113], reported that the esterification of bio-oil reduced the percentage of organic acid from 11.49% to 2.3% and the percentage of esters was increased from 3.23% to 26.26. The catalytic esterification improves the bio-oil stability by reducing the water content and dynamic viscosity, and by increasing pH, density, and calorific value.

4.5. Catalytic Cracking (Zeolite)

The produced bio-oil has the highly oxygenated compounds and the catalytic upgrading method is used to improve bio-oil by deoxygenation process. The principle of catalytic upgrading is treating the hot vapor prior to quenching with a suitable catalyst to crack the desirable organic compounds and from a less oxygenated liquid. The various types of catalysts such as solid acids, zeolites, silicalite, silica-alumina, alumina, FCC catalysts as well as metal oxides, copper chromite, zinc oxide, zirconia, and ceria have been used in the catalytic upgrading of bio-oil [114-117]. Either the catalyst can be treated with biomass or can be supplied with hot vapor externally. The catalytic upgradation of bio-oil involves processes

such as cracking, deoxygenation, cyclization, oligomerization, aromatization, isomerization, alkylation, and polymerization [118]. The use of zeolite as a catalyst was found to be very promising because of its unique porous structure. The ZSM-5, a popular petroleum catalyst as well as used as a catalyst for bio-oil upgradation produces bio-oil with a desirable phenolic compound and with a low percentage of acids [119]. The application of zeolite for bio-oil production in different pyrolysis reactor and pyrolysis condition was reviewed by Isahak et al. [120].

Garba et al. [121] experimented with varying concentrations of ZMS-5 with biomass. The experiment revealed that the catalyst with 15% of biomass gives the maximum bio-oil yield of 49.4% as compare to non-catalyst pyrolysis it was only 21.2%, at a temperature of 500 °C. Nevertheless, it was reported that the yield of bio-oil, gas, and char was slightly influenced by the zeolite structure but the chemical composition of the bio-oil was highly dependent on the structure of the catalyst [122]. Similarly, Kurmi et al. [123] reported that the pore size and acidity of the catalyst have a profound effect on the product distribution, coke formation, and deoxygenation rate. Furthermore, the produced bio-oil from catalytic pyrolysis mainly gives phenolic, ketones, aromatic, and olefins compounds [121-124]. The study by Chaihad et al. [125] revealed that zeolite with high alumina content, convert the oxygenated compounds into 60-100% of aromatic hydrocarbon. Furthermore, the catalyst was regenerated by the calcination process and the activity of the regenerated catalyst found the same with the fresh one. The application of alkali-metal based catalysts such as Na₂CO₃ and K₂CO₃ and Ni-based catalyst such as Ni/SiO₂-N found to be most effective in the tar destruction formed on the pyrolysis reactor during the process. It was reported that the carbon deposition on the structure of the catalyst obstructs the activity of the catalyst [126, 127]. However, the limitation of zeolite cracking is addressed in the next section.

4.6. Hydrodeoxygenation

The zeolite cracking has some disadvantages, namely, it lowered the H/C ratio of bio-oil and excess carbon saturation on the surface of the catalyst which results in a short life of the catalyst. These limitations hinder the zeolite cracking process of upgrading the bio-oil. To overcome this issue the Hydrodeoxygenation (HDO) found to be promising, as it involves the processing of bio-oil with high pressure H₂ (100-200 bar), high temperature (300-400°C) and removes oxygen partially in the form of water to produce hydrocarbon. HDO involves chemical reactions such as decarboxylation, hydrogenation, hydrocracking, hydrogenolysis, and dehydration [128]. HDO increases the H/C ratio of bio-oil and produces high-grade bio-oil. Another advantage of the supply of hydrogen is to prevent the coke deposition on the surface of the catalyst [129, 130].

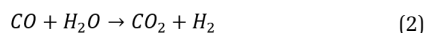
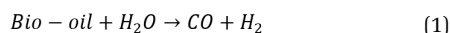
Moreover, to study in detail about the HDO mechanism and its reactions with bio-oil, HDO of model compounds are selected rather than the whole bio-oil. Because there are only some active compounds available in bio-oil which affects the stability of bio-oil, so these types of active compounds are selected for HDO. The selected model compounds are such as guaiacol, anisole, phenol, veratrole, phenolic monomers, furans, dimers, and carboxylic acids

to produce hydrocarbon mainly cyclohexane [131-134]. The different types of catalysts were studied to improve the HDO process, such as sulfide MoS, CoMoS, NiS, NiMo/Al₂O₃, and CoMo/Al₂O₃, some metal catalyst such as platinum, rhodium, ruthenium, and nickel [133]. Furthermore, the performance of bi-functional catalysts such as platinum loaded HYzeolite [131], bimetal catalyst Ni-Mo/ZrO₂-Al₂O₃ [135] was also tested and it was found that bi-functional catalyst can produce high-grade bio-oil over mono-functional catalyst [132-135]. However, Patil et al. [135] studied the effect of bimetal catalyst Ni-MO/ZrO₂-Al₂O₃ (mixed oxide) on the deoxygenation of bio-oil model compound guaiacols. It was observed that the 100 % guaiacols conversion was achieved with 45.3% phenol at temperature 330°C and 30 bar H₂ pressure. It was observed that along with phenol, some percentage of cyclohexane and hydrocarbon were also recovered from the HDO of guaiacols.

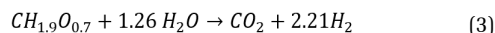
In recent years, the supercritical solvents are being studied as reaction medium in HDO [136-140]. The supercritical solvent helps in the limitation of hydrogen solubility in HDO. Recently, Shafaghat et al. [141] performed HDO of bio-oil in methanol, ethanol, 2-propanol with using the HBeta catalyst supported Ni catalyst. (Ni/Beta). The methanol gave a maximum degree of bio-oil deoxygenation and the heating value of crude bio-oil was increased from 12.61 MJ/kg to 24.17 MJ/kg. While Xiong et al. [142] also experimented HDO whole bio-oil with Raney Nickel and zeolite supported Ru catalyst, found that the upgraded oil has a low yield of organic liquid. Whereas, Si et al. [134] suggested that two stage hydrodeoxygenation and in situ hydrogenation are the better way to upgrade bio-oil via HDO.

4.7. Steam Reforming

The application of hydrogen as fuel and raw material in the chemical industry is attracting the world's attention, as it is green fuel. Biomass has the potential to accelerate the hydrogen production by many routes such as gasification, pyrolysis, dark fermentation, direct/indirect biphotolysis, and photo fermentation, etc. [143]. The gasification coupled with water and gas shift is the widely accepted process for hydrogen production but now the catalytic steam reforming of bio-oil produced from the fast pyrolysis of biomass is also receiving great attention. The catalytic steam reforming process is carried out at a temperature of 750-850°C and the most commonly nickel-based catalyst is used [144-145]. The process completes in two reactions, as follows,



The maximum hydrogen produced from steam reforming of bio-oil was 17.2 g of hydrogen per 100 g of bio-oil [146]. The overall reaction of biomass pyrolysis to reactive vapor and formation of H₂ as follows.



The steam reforming of single or model compounds of bio-oil or real bio-oil carried out to produce hydrogen. The different model

compounds of bio-oil such as acetic acid, acetone, phenol, and glycerol were used for steam reforming [147-151].

Besides, some notable research related to steam reforming of complex bio-oil compounds and real bio-oil is presented here. The reaction temperature, steam to carbon ratio, and retention time have a profound effect on the steam reforming of bio-oil. Mei et al. [152] reported that a maximum of 79.8% of hydrogen yielded from steam reforming of m-cresol (model compound of bio-oil) at a temperature of 850°C, the retention time of 5h, and steam to carbon ratio as 5:1. Whereas, Trane-Restrup et al. [153] showed that the yield of H₂ and conversion was increased with increasing steam to carbon ratio in the range of 1.6 to 8.3. However, Valle et al. [155] reported that the optimum carbon ratio of 6, gave a maximum H₂ yield of 87-93%. Presently steam reforming of bio-oil is found viable option to produce hydrogen from bio-oil but some challenges are still there to be studied such as the performance of the catalyst in terms of reactivity and stability, coking, cost of catalyst.

4.8. Supercritical Fluids

The solvents such as ethanol, methanol, and water were used as supercritical fluids for the upgradation of bio-oil. The supercritical fluids (SCFs) have the ability to dissolve materials, which are not normally soluble in the liquid or gaseous phase of the solvent. As well as it has unique properties such as liquid-like density, gas-like diffusivity and viscosity, and high rates of mass and heat transfer [93]. The supercritical fluids can be used as reaction condition in the production of bio-oil mainly in the process of hydrothermal liquefaction of biomass as well as it can be used for the upgradation of bio-oil. The SCFs upgrading of bio-oil is also performed in the presence of catalyst and solvent such as ethanol, methanol, CO₂, and water [156-159]. When SCFs are performed with acid catalysts and alcohol then it is called esterification of bio-oil with the supercritical condition [160]. SCFs upgrading method is used to increase the heating value of the bio-oil and to lower the viscosity. Duan and Savage [157] reported that the heating value of algal bio-oil was increased to 43 MJ/kg and the total acid number decreases from 256 to 25 using the supercritical water upgrading method. However, Zhang et al. [138] investigated the esterification of bio-oil compounds in supercritical ethanol. It was reported that at supercritical condition, all carboxylic acid (42.19%) from the crude bio-oil transformed completely into esters. Moreover, Prajitno et al. [161] performed an experiment on bio-oil upgradation in supercritical ethanol, without employing external catalyst and hydrogen. It was revealed that the upgraded bio-oil properties such as higher heating value 34.1 (MJ/kg), TAN- 4.8 (mg KOH/g), and water 1.6 (wt%), was improved as compared to raw bio-oil properties HHV- 24.3 MJ/kg, TAN-69.4 mg KOH/g and water-14.0 wt%, respectively. Recently, Shafaghat et al. [141] found that the combination of HDO and supercritical fluid system increase the heating value of bio-oil and improves the deoxygenation degree. The heating value of upgraded bio-oil was increased from 12.61 MJ/kg to 24.17 MJ/kg and the degree of bio-oil deoxygenation (42.71%) was highest while using methanol as SCFs. Table 5. explains the process description of different bio-oil upgrading methods along with the media used and limitations of each method.

Table 5. Bio-oil Upgrading Methods

Upgrading methods	Process description and effects on bio-oil	Media used	Limitations	References
1) Hot vapor filter	It removes char and ash particle from the vapor.	Porous sintered steel (pss) sintered metal powder, sintered ceramic powder, ceramic, flexible ceramic cloth, rigid sintered, stainless steel, glass wool, 0.1 μ m polycarbonate film	Reduces oil yield, Increases iron content, and continuous increase in pressure drop during operation.	[79, 82]
2) Solvent addition	Improvement in homogeneity of the bio-oil. Increases in lower heating value of bio-oil. Decreases viscosity and density	Three types of alcohol used namely methanol, ethanol and isopropanol	Decrease in the flash point of the bio-oil. Solvent addition mechanism is still complicated	[86, 162]
3) Emulsification	Increases calorific value and reduces water content (entire composition of bio-oil converted into fuel)	Emulsifiers used- Span 20, Span 80 and Span 100. Span 85, Tween 85, Span 60, Brij 72 and hypermer B246. Tween 80, and Lignin	Problem of stability and corrosion Emulsifier and co-emulsifier are expensive and refining of bio-oil from emulsion is a problem	[163, 164]
4) Esterification	It removes carboxylic acids from bio-oil to form esters. Improve stability, reduces corrosiveness, acid number and increases lower heating value.	Solid acid catalyst, solid base catalyst, Zeolite, ionic solid and liquid catalyst and aluminum silicate	Low oil production and poor performance	[113]
5) Catalytic Cracking (zeolite)	It eliminates oxygen-containing compounds from the bio-oil during the pyrolysis process as it helps to improve the bio-oil properties such as acidity, water content, viscosity and calorific value.	Calcined Dolomite, Na ₂ CO ₃ , K ₂ CO ₃ , Ni-based catalyst Ni/SiO ₂ -N, and ZSM-5, HZSM-5, FCC SAPO-11, H-mordenite, M ₈ AP0-36, H-Y, Z _n HZSM-5, Na ₂ CO ₃ /Al ₂ O ₃ , K ₂ CO ₃ , MgO and Ca(OH) ₂	Lowered the H/C ratio, i.e produces low grade bio-oil. Short life of catalyst and reactor clogging	[129, 130]
6) Hydrodeoxygenation	Removes oxygen using pressurized hydrogen, It increases the heating value, reduces the viscosity of bio-oil	sulfide Fe, Co, CoMo, NiMo, NiCu, NiMo/Al ₂ O ₃ and CoMo/Al ₂ O ₃ platinum, rhodium, ruthenium and nickel	Required high pressure hydrogen High cost, low hydrogen utilization efficiency	[133]
7) Steam reforming	Used to produce hydrogen by steam reforming of bio-oil.	Metal catalysts (base and noble)- Ni, Rh, Pt, Pd, Co, Cu, Ir, Fe Supported materials MgO, MgO-Al ₂ O ₃ , CeO ₂ , ZrO ₂ , Calcite, Dolomite, Al ₂ O ₃ Zeolites-Y, ZnO,	Reactivity and stability of catalyst is very short, coking and cost of catalyst,	[148, 149]
8) Supercritical fluids	It increases the higher heating value of bio-oil, it also helps to lower the acid number of bio-oil	Ethanol, methanol, CO ₂ and water used as solvents Catalyst used- Pt/C, Ni	High cost of the solvent.	[157]

5. Applications of Bio-Oil

The bio-oil as green fuel gained popularity worldwide from the last three decades however, recent development in production and upgradation makes scientific people believe it as a forerunner to replace conventional fuel. The bio-oil produced from agricultural waste, forest residues, and urban organic waste has a wide range

of applications. Despite some limitations, the bio-oil as fuel can be used directly to produce heat, electricity, and engine application as well as in the chemical industry. The bio-oil is can be used as fuel in industrial boiler and furnaces. The furnaces and boiler are used mainly to produce heat at the industry level. The flame combustion test shows that bio-oil can be used directly in a boiler to replace heavy and light fuel oil [35]. The bio-oil requires a

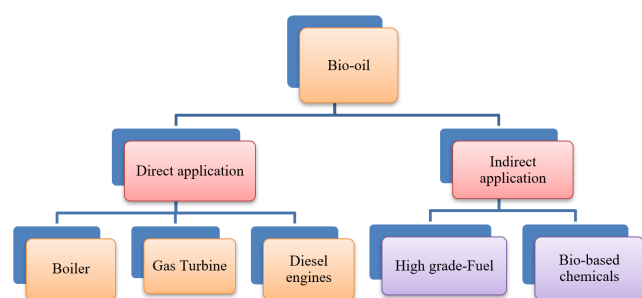


Fig. 3. Applications of bio-oil.

stoichiometric mass air/fuel ratio in between 5-7 for combustion, which is half of the standard fuel oil. As well as it has a longer flame than the standard fuel oil [165]. To use bio-oil as fuel in burner or furnace, it required some conditions such as support fuel to startup and shutdown, low concentration of solid particles (< 0.1 wt.%), as well as slight modification in burner design, such as parts in contact with bio-oil, should be made of stainless steel or any other corrosion resistance material [37]. The Red arrow product pyrolysis plant, United States, has used bio-oil as fuel for heat generation for more than 10 years. The 5 MW_{th} swirl type burner was designed and used for the combustion of bio-oil, char, and gasses released from the plant [166].

The heating value of bio-oil is nearly half of the diesel, though it can be used directly in a diesel engine or gas turbines [167]. The study shows that bio-oil performed well when tested in a diesel engine [43]. However, Bridgwater (168) has done a successful run of 400 h of the modified dual-fuel engine with 250kWe capacity. In an experiment, a single cylinder engine runs on bio-oil and found that for proper ignition, raw bio-oil must be preheated to 55°C. It was also reported that raw bio-oil performed well in the low speed engine than medium speed engine [4]. Recently, bio-oil is also used as fuel in co-firing with coal, heavy fuel oil, light fuel oil, and natural gas in a variety of applications such as gas turbine, boiler, and power units [169]. Besides, bio-oil is complex mixtures of water and various organic compounds, and it can be used for the production of food flavorings, aromatic, olefins, resins, adhesives, agrochemicals, and fertilizers in the chemical industry [4, 94]. Fig. 3. shows the scheme of bio-oil application, directly as fuel in the boiler, gas turbines and, diesel engines and upgraded or processed bio-oil into high-grade fuel and bio-based chemicals.

6. Environmental Impact of Bio-Oil Production

Recently, more concern is being given to the environmental impact of biomass generated fuel. However, it is well known that the biomass is green and CO₂ neutral fuel as well as the fuel produced from biomass such as bio-oil, biochar, etc. also cited as carbon neutral because the amount of CO₂ emitted during the combustion of bio-fuel is same as the amount of CO₂ consumed by biomass during the growth. Despite this, many studies reported that bio-energy conversion into fuel does not guarantee the zero impact on the environment or it is completely environmentally friendly

[170-172]. Therefore life cycle assessment (LCA) of bio-oil production and upgradation is found important to study the overall environmental impact of it. However, the LCA of any system or technology aims to inform the policymakers about the best option which is environmentally friendly [173]. The LCA of biofuels was studied by analyzing impact factors such as global warming potential (GWP), abiotic depletion (ADP), non-renewable energy demand (CEDnr), acidification (AP), eutrophication (EP) [174-176].

The fast pyrolysis process for bio-oil production involves various operations such as transportation of raw biomass feedstock, drying, heating of feedstock, condensation of vapor, upgradation, storage, and transportation of produced bio-oil. To perform these operations conventional fuels may be used. It was predicted that the bio-oil production process produces negative environmental impacts [177]. Besides, Han et al. [178] reported that bio-based gasoline requires an extra 32.43% of the total energy than conventional gasoline. However, Chan et al. [175] studied the LCA of two bio-oil production methods i.e. fast pyrolysis and hydrothermal liquefaction. The author reported that for the production of 1 kg of bio-oil from empty fruit bunch biomass, a net 4.46 and 2.29 kg CO₂ equivalent generated from fast pyrolysis and hydrothermal liquefaction method, respectively. It was also reported that due to the high energy requirement for the operation of the fast pyrolysis process, caused 50% more GWP impact compared to HTL. Furthermore, LCA of extraction of particular compounds from bio-oil was also studied by Chan et al. [176]. The author found that the extraction of every kg of phenol from bio-oil produced from palm kernel shell via the hydrothermal liquefaction process produces 42.69 kg of CO₂ equivalents.

The bio-oil as fuel can be used in many applications such as electricity generation, heating, and fuel for engines. Bio-oil as fuel in the replacement of conventional fuels reduces greenhouse gas emissions. Fan et al. [179] conducted a study of electricity generation using bio-oil, electricity generation was achieved through the combustion of bio-oil in conventional fossil fuel power plants. The study estimated that 77-99% of GHG emissions were reduced when bio-oil was used as fuel for combustion for power generation compared to fossil fuel. The percentage of GHG emissions may vary depending upon the type of feedstock and combustion technologies used.

Dang et al. [180] studied the LCA of fast pyrolysis and upgradation (hydro treating) of 1 MJ bio-oil produced from corn stover. The environmental benefits were analyzed in terms of non-renewable energy demand and Global Warming Potential (GWP). The study revealed that for the production of 1 MJ bio-oil, 0.39 MJ net non-renewable energy demand (i.e. reduction of 67.5%) and 28.83 g CO₂-eq (i.e. reduction of 69.1%) net GWP compared to conventional gasoline and diesel 1.2 MJ net non-renewable energy demand and 93.22 g CO₂-eq net GWP were achieved.

The electricity consumption during the fast pyrolysis process is the principal cause for the reduction of overall environmental impact. Peters et al. [181] studied and compared the LCA of upgraded bio-oil (synthetic bio-oil) produced from hybrid polar with the equivalent fossil fuel such as gasoline and diesel. The result of the study showed that with the production of 1 MJ of synthetic bio-oil 54.5% of greenhouse gas (GHG) was saved as compared to conventional gasoline and diesel. It was also reported that the

impact of synthetic bio-oil lower than that of the fossil fuel for abiotic depletion (ADP) and non-renewable energy demand (CED_{nr}) and higher for acidification (AP) and eutrophication (EP).

7. Discussion

From the detailed overview of different bio-oil upgrading methods, it is clear that the cost-effective and efficient method for bio-oil quality improvement has not been developed so far, thus there is a wide opportunity for researchers to develop such a new method. To date, more emphasis is given to produce bio-oil using high efficient reactors or methods and different biomass and it helps people around the globe to realize the potential of bio-oil or pyrolysis oil as fuel. However, from the last ten years researchers concentrating on the quality improvement of bio-oil to replace and compete with conventional fuels in the market. The physical method i.e. filtration of bio-oil upgrading is not found satisfactory, because it only helps to lower the char and ash content of bio-oil, or helps to improve the viscosity of the bio-oil. But the bio-oil remains with high oxygen content and low heating value. The bio-oil is highly unstable and immiscible with hydrocarbon fuel, confines its use in engines. It can be used in engines but it requires a pilot fuel for the ignition. The heating value of the bio-oil is the main reason to be considered before using it as fuel, the addition of a polar solvent such as methanol, showed significant improvement in the bio-oil stability and heating value [45]. The blending of bio-oil with co-solvents (alcohol) and other sustainable fuels like bio-diesel, showed a promising path to improve the bio-oil quality [182].

As, the upgrading methods such as solvent addition, emulsification, and esterification showed some significant results to improve the bio-oil quality, but some problems like low compatibility, low efficiency, and high process cost make these methods unfeasible. It was found that the post-production cost of bio-oil is keeping bio-oil applications away from commercialization. Therefore, from the recent literature, it was observed that the integration of different upgrading methods and separation techniques of bio-oil would be the promising option to produce bio-oil with high-grade quality. However, bio-oil separation techniques possess advantages such as simple and easy operation, low investment, and obtaining valuable chemical compounds. From this review paper, hydrodeoxygenation methods found promising for improving the bio-oil quality in terms of heating value, process efficiency. The separated compounds from bio-oil e.g. acetic acid, carboxylic acids, phenol, furans, and dimers, etc. can be used to produce hydrogen as an energy source in the upgradation process of bio-oil i.e. hydrodeoxygenation [67]. Moreover, the cost of hydrodeoxygenation can also be minimized by applying two stage hydrodeoxygenation and in situ hydrogenation [134]. The blending of bio-oil with supercritical methanol, ethanol, isopropanol, etc. increased the heating value of bio-oil from 17.51 to 28.85 MJ/kg [183]. Therefore, the blending of supercritical fluids or bio-diesel with bio-oil is also recommended by keeping the cost of the process into consideration. It needs to develop such an integrated method which is economical and can produce bio-oil with equivalent to hydrocarbon fuel.

8. Conclusion

In this paper, the recent development of bio-oil upgrading and separation techniques were reviewed. The fast pyrolysis and hydrothermal liquefaction processes are the convenient and easy way for bio-oil production from biomass. The separation of specific compounds from bio-oil was achieved by different separation techniques such as distillation, solvent extraction, and column chromatography has some limitations. However, a new technique such as molecular distillation and supercritical fluids extraction is found with great potential and more efficient than the conventional separation techniques.

The obtained model compound such as guaiacol, anisole, phenol, phenolic monomers, furans, dimers, and carboxylic acids is can be further upgraded to obtain hydrocarbons using various upgrading methods or can be used as value-added chemicals. The bio-oil upgrading methods include physical, chemical, and catalytic processes. The physical method like filtration is used to lower the viscosity and molecular weight, which helps in increasing the stability of bio-oil while storing. Solvent addition and emulsification were also improved bio-oil stability by adding solvents and surfactants respectively, but it seems to be short-term approaches. However, the esterification process is found as an economical method but has limitations such as low oil production and poor performance. The catalytic cracking methods such as hydrodeoxygenation, zeolite cracking, and steam reforming seems to promising methods for bio-oil upgrading since it is been used in oil refineries by many years and recently many research experiments were carried out on biomass fast pyrolysis and found satisfactory results. The steam reforming is used to produce synthesis gas or H_2 from hydrocarbon fuels. The catalytic upgrading methods such as HDO and zeolite cracking and supercritical fluids found very promising, however, it has some limitations i.e. high cost, poor durability, catalyst deactivation, and reactor clogging. Therefore, the commercial application of bio-oil is not possible yet, but in the near future, it could be possible after reducing the upgradation (post-production) cost of bio-oil. The life cycle assessment of bio-oil production and upgradation is essential to bring the product at an industry level.

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Author Contributions

N.L.P (Assistant Professor) supervised the student, wrote and edited the manuscript. A.S.P. (Ph.D. Student) conducted the research and investigation process and wrote the original draft.

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