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REVIEW

A Review on Bio-oil Upgradation by using Physico-chemical Methods

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ABSTRACT

Recently, the fuel crisis has been getting worse every day, impacting the economy of the society and the nation as well as aggravating the environmental imbalance by rising carbon levels and air pollution However, green and renewable bio-oil can provide a solution for affordable energy and environmental safety but the drawbacks of bio-oil include its higher viscosity, polarity, high molecular weight due to the high oxygen content, tar content, acidity in nature, high molecular weight due to its high viscosity and moisture content. As a result, bio-oil cannot be used directly in engines or high energy applications and must be upgraded for those uses. This study concentrated on ways to enhance the quality of bio-oil utilizing physical and chemical upgrading techniques, including hydro-cracking, hydro-treatment, hydro-deoxygenation, esterification, emulsification, and steam reforming. The bio-oil industry and bio-oil-based research for the creation of clean energy fuel will both be solved by this study.

KEYWORDS

Waste material, bio-oil, up-gradation, chemical methods, physical method.

INTRODUCTION

As a result of recent increases in energy consumption and the use of hydrocarbon fuels, we are currently experiencing an energy crisis (petrol, diesel, etc.). Due to the greenhouse gas emissions from these traditional fuels, they are expensive and have negative environmental effects [**1**]. Furthermore, biomass has the potential to produce clean and alternative fuels through thermo-chemical conversion processes like pyrolysis, gasification, combustion and liquefaction, which result in the production of bio-oil, charcoal and pyro-gases [**2**]. In fact, biomass makes up 77.4% of the world's renewable energy supply. Due to its low cost and simplicity of usage, pyrolysis—a type of heat breakdown that occurs in the absence of oxygen which has been considered a feasible method for converting biomass [**3**]. The pyrolysis operating conditions have a significant impact on the quality of the bio-oil and the output products. The raw bio-oil could not be used directly in diesel engines due to impurities in the bio-oil, such as tar content, moisture content, unnecessary viscosity and density due to oxygen content. The purpose of this work was to develop a superior bio-oil that contains little to no oxygen and can be used as a car fuel [**4**]. Bio-oil contains around 300 different substances. However, it was also noted in the literature that a high heating rate is also acceptable for the pyrolysis process and that it could be used to lower the O_2 content from the bio-oil. The majority of them have significant oxygen content, which has a negative impact on the qualities of bio-oil. Due to varied chemical compositions and groups, bio-oil has an oxygen concentration of 30–40 weight percent; the presence of oxygenated compounds increased the acidity and corrosiveness [**5,6**].

These highly oxygenated groups also have an impact on viscosity because some substances encourage polymerization, which significantly increases oil viscosity [**7**]. Several studies have been published that look at the pyrolysis behavior of various feedstock's [**8,9**] as well as the effects of hydro-treating on the properties of bio-oil [**10, 11**]. The instability of bio-oils during storage is a significant issue since it affects their viscosity, heating value and density. It is necessary to upgrade bio-oil to break the

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interactions between the various reactive hydrocarbons and improve stability which provide consistent bio-oil mixing in petro-diesel products. Three alternative methods can be used to carry out this upgrading: catalytic hydro-treating, also known as hydro-deoxygenation (HDO), which primarily involves de-carboxylation, hydro-cracking, hydrogenolysis, and hydrogenation reactions [**12**].

Bio-oil has a heating value that is less than half that of regular fuel oil. Because the bio-oil contains oxygen and water, it has a poor heating value. The quality of the oil fuel is enhanced and the nutritional value of bio-oil is increased by removing water and oxygen. The single most important step in increasing and maintaining the characteristics of bio-oil for use as a transportation fuel is the removal of oxygen [**13**]. Another study discovered that bio-composition oil's is important for its application in diesel engines. For example, bio-oils containing hydroxyl radicals are preferred to those containing sugars for applications using diesel engines [**14**].

To make bio-oil practicable for use in a variety of applications, it is vital to continue developing the products made utilizing these approaches. Catalytic materials are essential to the catalytic upgrading of bio-oil, which can be accomplished in a variety of ways, including hydro-treating, hydro-cracking, hydro-deoxygenation, emulsification, steam reforming, and esterification [**15**]. There are several ways to improve bio-oil. Each technique offers a unique set of advantages and disadvantages. Physical procedures like solvent addition and emulsification seem to be temporary fixes for improving bio-oil [**16**].

The majority of chemical operations require high temperature and high-pressure processes, which raises the cost of upgrading significantly. At atmospheric pressure and low temperatures, esterification is possible, but it has little impact on denitrogenation. Hydro treating seems like a viable alternative because it has been used in oil refineries for a long time and the technology is well established, but more work needs to be done to address the issues of cocking and catalyst deactivation. Academics from all over the world are interested in improving bio-oil, but nothing has been done in this area and opening up a new line of inquiry [**17**].

Table 1. The main causes, effects and solutions of bio-oil.

Drawback	Cause	Effect	Solution	References
High water content	Thermal cracking, feed water	Complex impact on stability and viscosity Water content increases have an adverse impact on calorific value, density, stability, and catalyst PH.	Phase separation of bio-oil etc.	18
High viscosity drop	Bio-oil chemical composition	Gives high equipment costs for pressure-increasing equipment and high biomass pumping costs	Hydro-cracking Catalytic cracking Solvent addition etc.	59
Compositions with a high oxygen content	Stability issues	Non-mixable with hydrocarbons	Hydro deoxygenation	19,20
Low H:C ratio	The H:C ratio of biomass is low.	The transition to hydrocarbons is more challenging	Hydro treating Hydrofining etc.	22
Acidity	Organic acids derived from the degradation of biopolymers	Corrosion of pipes and containers	A chemical extracted from bio-oil through esterification.	21,22
High Oxygen content and viscous	Poor stability	• Increased oil yield • Improved fuel quality (lower O content and viscosity)	Supercritical fluid	23

BIO-OIL PRODUCTION TECHNOLOGY

Pyrolysis technique

The pyrolysis technique converts biomass into bio-oil, char, and gases depending on the pyrolysis conditions. Pyrolysis is a promising technology for using biomass. Pyrolysis is the thermal disintegration of materials in the absence of oxygen. Pyrolysis may be a viable method for converting lignocellulosic biomass since the bio-oils produced from biomass pyrolysis can be used to do so [**24,25**]. According to research by higher bio-oil yields were obtained from biomass feedstocks with higher volatile matter, higher heating value, carbon, nitrogen, and reduced moisture content, ash, fixed carbon, carbon, nitrogen, hydrogen, oxygen, and sulphur. Pyrolysis is the destructive distillation of organic substances at higher temperatures without oxygen; it can be divided into two categories: slow pyrolysis and quick pyrolysis. Bio-oil, charcoal, and pyro gas are the pyrolysis' output products. The type of biomass used as input and the heating temperature and rate have a significant impact on the generation of bio-oil [**26, 27**].

Types of Pyrolysis

Fast pyrolysis

During the fast pyrolysis procedure, the organic feedstock is rapidly heated at a high heating rate without oxygen. During the breakdown process, char and vapors are created. Upon the condensing of the vapors, a dark brown liquid is produced. Rapid pyrolysis is a challenging process that can be managed to produce higher yields of liquid products.

Rapid pyrolysis produces 10–20% non-condensable gases, 60–75% liquid bio-oil, and 15–25% char. Non-condensable gases can be recycled back into the process, and bio-oil and char can be used as fuel [**28,29**]. The pyrolysis reactor, which is in the center of the pyrolysis process, is crucial to the quick pyrolysis process.

Slow pyrolysis

Slow pyrolysis involves heating materials at a rate of 5–10 °C/min. In this process pyrolysis outputs are bio-oil, charcoal, and pyro gases but by this technique, bio-oil production will be less, and charcoal and pyro gas output will be increased.

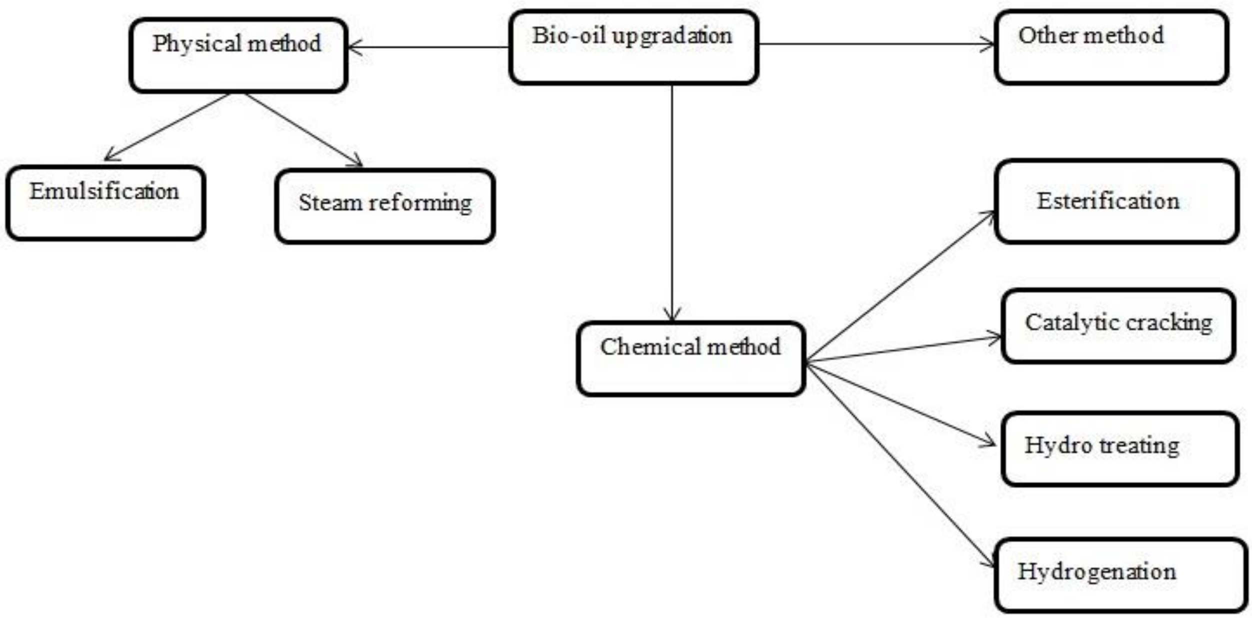

Fig. 1. Flowchart for improving bio-oil by using a different processing method.

BIOMASS CONVERSION METHODS

After discovering acceptable biomass sources determining the optimal procedure for converting biomass to biofuels is extremely difficult. There are numerous technologies available for turning biomass into bio-oil. There are four types of thermochemical conversion of biomass: pyrolysis, gasification, combustion and liquefaction. The thermal decomposition of organic components of biomass in pyrolysis begins at 350-450 °C and advances to 700-800 °C in the absence of air/oxygen. Long carbon chains paired with hydrogen and oxygen degrade into smaller chains in the form of gases, condensable vapors and solid charcoal under pyrolytic conditions [**30**].

The thermochemical method's byproducts, such as bottom ash, solid leftovers, and metal or non-metal slags, are recyclable and reusable. When compared to landfills, the output of greenhouse gases and other pollutants is significantly reduced, and it is anticipated that around one ton of CO_2 is retrieved. According to life cycle assessment studies, waste-to-energy technology has a low environmental impact and can be used as a source of energy [**31,32**]. The content and features of the biomass have a significant impact on the process parameters, reaction rate, yields, and quality of the conversion products. The primary features of biomass can be determined by examining its proximate and ultimate composition [**33**]. Also, the increased moisture content of biomass requires more energy to dry the feedstock before thermochemical conversion, resulting in a lower heating value of the biofuel output. Lower moisture, oxygen and ash concentrations can improve the calorific value of the conversion result [**34**]. This review focuses on the outlook for different thermochemical treatment techniques for municipal solid waste, including organic, paper, plastic, and mixed municipal solid waste and the upgradation techniques and catalysts for improved fuel production.

A statistical review of the use of Thermochemical conversion of biomass conversion to bio-oil

The Web of Science (WoS) database was used for the analysis and the use keywords in conjunction with suitable syntax (search operator) to search for "thermochemical conversion, "pyrolysis", and "waste materials". The search from 2012 to 2022 resulted in 2500 published documents, indicating the extensive use of “Thermochemical conversion of waste material” all over the world in last decade. Moreover, VOS viewer was used to construct the term co-occurrence of the 2500 documents, which revealed the following key clusters: thermochemical conversion of waste material.

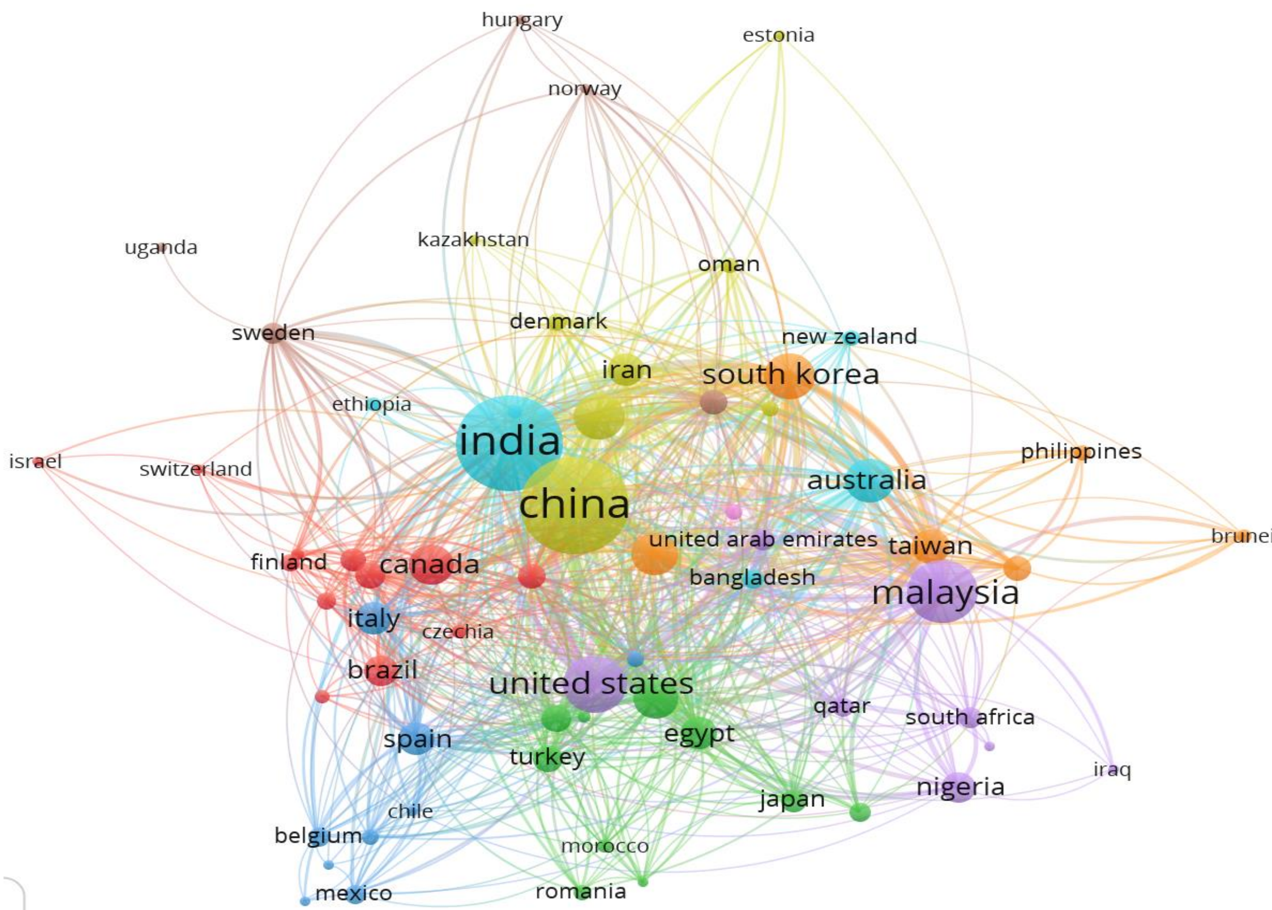

Fig. 2. VOS-viewer network visualization of terms associated with the thermochemical process of Biomass waste.

BIO-OIL PRODUCTION

Bio-oil is a multi-component organic material mixture derived from several sources. It is predominantly composed of oxy-compounds such as acids, aldehydes, ketones, esters, phenols, alcohols, and ethers. Because of the diverse materials and processing procedures employed in its manufacture, the components of bio-oil differ [**35**]. They can dissolve in bio-oil in polar solvents like methanol and acetone, but not in fossil fuels due to their high oxygen concentration. During the storage and transit of highly reactive and thermally unstable oxy-compounds, unintended reactions might occur. As a result, bio-stability oil suffers tremendously and its utility suffers; therefore, the stability and combustion properties of bio-oil should be improved by lowering the water and oxygen levels [**36,37**]. The following features of bio-oils make them unsuitable for fuel applications [**38**].

1. A high oxygen concentration and, as a result, a poor heating value
2. Water content is high.
3. Very high viscosity
4. Corrosiveness is extremely high (acidity)
5. Nitrogen content is very high.
6. Instability due to thermal and chemical factors

Composition and properties

Water and oxygen content

Due to its high structural water content, as well as its highly viscous and acidic nature, bio-oil is a somewhat difficult fuel to burn. Whereas a high-water content (between 15% and 35% by weight) reduces porosity, making it simpler to transfer, pump, and atomize, it also lowers the higher heating value (HHV) [**39**].

Stability and viscosity

Increased viscosities are generally undesirable in fuel systems because they can result in poor atomization, leading in incomplete combustion; the extra injection pressure required may also cause the injector pump system to wear down faster [**40**].

Alkalinity

The high concentration of carboxylic acids in bio-oil results in a total acid number (TAN) of 50–100 mg KOH/g bio-oil and a pH of 2-3, making it extremely corrosive to aluminium, copper, low carbon steel, carbon steel and other metals [**41**].

NEED OF CHEMICAL TREATMENT

Chemical treatment can improve bio-oil quality by increasing heating value while decreasing viscosity, density and moisture content. The elimination of oxygen from bio-oil is the single most important step in stabilizing and improving its qualities for future use as a transportation fuel, and the high oxygen concentration in pyrolysis oil is the most significant barrier to its utilization. Bio-oil has a high moisture content, is quite acidic, and contains a lot of oxygen. To remedy these flaws, bio-oil requires an additional procedure known as upgrading, which removes oxygenated components and improves final properties allowing it to be used as a substitute for petroleum-based fuels [**42**]. Because of its high oxygen concentration, bio-oil loses value as a fuel, causing a slew of issues with consumption and administration. Bio-oil has a poor energy density, is unstable, and is not miscible with hydrocarbons due to its high oxygen concentration [**43**]. Carlson observed that, when compared to classical pyrolysis products, those generated by catalytic fast pyrolysis are more stable and contain less oxygen [**44**]. The bio-oil is completely depleted of oxygen using water, either as a natural component of the bio-oil or as water produced by the condensation processes that occur during heating. The informational points for this line state that bio-oils' high oxygen content cause them to have some undesirable properties, such as a poor heating value, an incompatibility with conventional fuels and a high viscosity. Storage can alter the viscosity, heating value, and density of bio-oils since some of the organic molecules they contain are very reactive. This poses a serious problem for bio-oils. For instance, ethers, acetals, and hemiacetals are produced when ketones, aldehydes, and organic acids are combined [**45**].

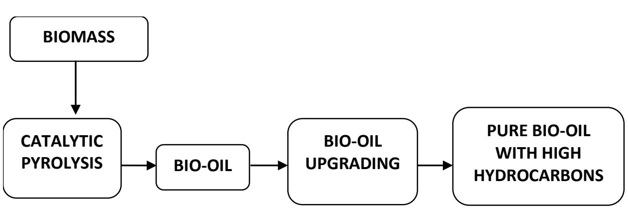

Fig. 3. Upgradation routes of bio-oil.

BIO-OIL UPGRADING

However, bio-oils produced through liquefaction are not suitable for conventional engines because, in comparison to pyrolysis oil, they are mostly composed of hydrophobic molecules with lower viscosity and higher solubility. As a result, bio-oil upgrading technology has improved greatly to enhance the fuel characteristics for real-world applications. A possible technique for improving bio-oil is hydro-treatment, which uses hydrogen gas to deoxygenate, fracture, and/or isomerize bio-oil [**46**]. While supercritical fluids can be used to fractionate the mixture species in bio-oil with high pressure and/or temperature, esterification can be employed to improve the quality of bio-oil under mild reaction conditions [**47**]. For the conversion to be effective, high temperatures (above 300 degrees Celsius) and either a lack of oxygen or extremely low oxygen levels are needed [**48**]. This cheap and abundant biomass can be used to make bioenergy and chemicals in a way that is both economical and responsible for the environment [**49**]. The bio-oil is highly oxygenated and chemically unstable. It must thus undergo upgrading procedures designed to enhance them, such as reducing the oxygen level or eliminating trash [**50**]. The high oxygen and water content of bio-oil accounts for its poor heating value. The pH of bio-oil is typically between 2-4 as a result of the presence of carboxylic acids. A further problem with bio-oil is its failure to retain stability during storage, which presents challenging conditions for shipping, storage, and processing equipment. Bio-oil becomes unstable because of depolymerization, which is brought on by the presence of highly reactive organic compounds [**51**].

Because of its high viscosity, high oxygenate concentration, poor stability, and low heating value, bio-oil produced from biomass pyrolysis is frequently of poor quality. The use of bio-oil must be upgraded. Catalytic hydro deoxygenation, catalytic cracking, catalytic steam reforming, catalytic esterification, and emulsification are some of the bio-oil upgrading techniques that were covered in this paper [**52**]. The two primary techniques for doing this are catalytic cracking and hydro deoxygenation. However, due to their complexity and high cost, many therapeutic methods are commercially unviable [**53,54**]. Using novel techniques for upgrading pyrolytic bio-oil is therefore crucial. The bio-oil products made using these techniques must be upgraded further in order to be used in varied applications. To catalytically enhance bio-oil, a variety of techniques can be applied, including hydro-treating and esterification [**55**].

CHEMICAL TREATMENT METHODS FOR BIO-OIL UPGRADATION

Different chemical methods are used to upgrade bio-oil, such as:

Esterification

Esterification is the process of converting alcohols and carboxylic acids found in bio-oils into esters, acetals, and ethers in the presence of an acid or base catalyst. According to studies, esterification with alcohol will reduce the acidity of the bio-oil and improve its quality and stability. High-quality fuels can be upgraded from bio-oil by esterification processes. With the use of proximate analysis, a gas chromatography-mass spectrometer (GC-MS), and a Fourier transform infrared (FT-IR) spectrometer, the bioactive composition and fuel efficiency of the final product were investigated. A heterogeneous acid catalyst system built of zeolites is one of the most often utilized catalysts for improving the bio-oil through the esterification process because of its suitably strong acidic sites, high surface area, and low cost. The process of bio-oil esterification enhances bio-oil with the aim of balancing acidity. Typically, it entails adding alcohol (30–100 weight percent), mild heating (60–120 °C) with a powerful acid catalyst, and distillation to remove water (20–40 weight percent). Because bio-oil and additional alcohols undergo two different types of equilibrium processes, water removal is required to achieve complete conversion [**56**].

Bio-oil is a promising renewable energy source whose primary components are waste products from industry and agriculture. The grade of bio-oil is still insufficient for use as a fuel, nevertheless. One method for enhancing bio-oil is esterification, which reduces viscosity and water content while raising heating value. This study's objective was to enhance bio-oil quality by kind and concentration acid catalyst [**57**]. To improve the quality of bio-oil, the process of esterification involves changing organic acids into esters. This method lowers the density of the bio-oil, makes it less corrosive, and increases its stability to produce high-grade fuel by adding polar solvents such ethanol, methanol, and furfural to the mixture and homogenizing it [**58**]. According to several research, adding ethanol or methanol straight to bio-oil lowers viscosity and increases heating value [**59**]. Under mild conditions, the catalytic esterification process combines ethanol with bio-oil and an acid catalyst (acetic acid) to make high-quality bio-oil. When bio-oil interacts with ethanol or methanol, a chemical event called esterification takes place [**60, 61**]. The improved bio-oil is more stable than the original bio-oil and even more stable than the heavily diluted bio-oil that failed to esterify. In addition to the material being corrosion-resistant, methanol has an impact. The product's quality increased as a result of dilution and upgrading [**62**]. In order to increase the stability of bio-oil and make hydrogenation easier, raw bio-oil was pretreated using esterification in varying concentrations of methanol [**63**].

Bio-oil analysis results after esterification

Bio-oil quality improvement has been given in Table 2 by using ethanol and acid catalysts (sulphuric acid and hydrochloric acid) [**64**].

Bio-oil after the esterification reaction with 50% ethanol (w/w) and acid catalyst types including H_2SO_4 (B1) and HCl (B2) was carried out with a variety of concentrations including 1% (K1), 3% (K2) and 5% (K3) shows a significant change in bio-oil characteristics such as decreasing kinematic viscosity, density, ash and acid numbers and increasing calorific value.

Table 2. Effect of type and concentration of catalyst on bio-oil characterization.

Pyrolysis bio-oil using catalyst	**Viscosity cSt @40°C**	**Density kg/dm3 @20°C**	**Calorific value MJ/kg**	**Water content wt%**	**Ash content wt%**	**pH**	**Acid no.**
Without catalyst	41.31	1.51	13.12	25	0.02	2.32	12.09
B1K1	3.06	1.20	20.17	0.83	0.0003	3.28	0.27
B1K2	3.10	1.24	16.65	0.84	0.0004	2.88	0.56
B1K3	3.13	1.26	15.90	0.85	0.0006	1.56	0.70
B2K1	3.03	1.23	18.31	0.84	0.0001	2.99	1.04
B2K2	3.07	1.23	17.23	0.85	0.0006	2.79	1.64
B2K3	3.22	1.25	15.23	0.86	0.0008	2.42	1.89

Hydro deoxygenation

By utilizing an appropriate catalyst, hydro deoxygenation (HDO) is a very practical method for upgrading bio-oil. The HDO method relies on the application of H_2 gas to eliminate the oxygen heteroatom and create H_2O. Hydrogen plays a significant role in saturating double bonds, which raises the fuel products' H/C ratio and enhances their quality in addition to eliminating oxygen from bio-oils. In their study published that looked into some of the drawbacks of adding sulphur before hydroprocessing. They came to the conclusion that the presence of H_2S reduced the hydro deoxygenation activity of the sulfided catalyst. The sulfied catalyst was mostly deactivated by the coke and high molecular weight compounds produced during the hydro-processing process; water produced during the HDO process also served as an inhibitor [**65**].

A two-step hydro-processing procedure was used, and the working temperature was raised from a low to a high range. This procedure was used to get rid of issues with reactor blockage and bio-oil polymerization at the beginning of the research. The difficulties with bio-oil polymerization have decreased as a result of these two steps [**66**]. The use of ex situ catalytic rapid pyrolysis and hydro-treating to produce low-oxygen bio-oil. The major objective of the study was to lower oxygen levels and oxygen content in bio-oil of various compositions. It was also carried out that after hydro-treatment, aromaticity and saturated hydrocarbon content values increased [**67**].

Due to various chemically reactive components, the raw bio-oil has impurities including phase separation, high viscosity, density and viscosity with aging issues. Nevertheless, following hydro-treating, all of these issues may be resolved and enhanced bio-oil characteristics can be achieved [**68**]. The high oxygen and water content of bio-oil lowers its ability to heat. The pH of bio-oil is typically between 2-4 as a result of the presence of carboxylic acids. The equipment required for transportation, storage, and processing must withstand extreme conditions due to the acidic nature of bio-oil. The inability of bio-oil to maintain stability while being stored is another problem. Bio-oil instability is linked to the presence of highly reactive organic chemicals that lead to re-polymerization. Moreover, hemiacetals, acetals, and ethers can all be produced by the reactions of organic acids, aldehydes, and ketones [**69,70**]. The most promising approaches, which are both economically possible, are catalytic cracking and hydro deoxygenation of bio-oil. Using catalytic cracking over zeolite catalysts, bio-oil can be improved (oxygen removed as CO2 and water) at atmospheric pressures and high temperatures (300–600°C) [**71**]. Catalytic hydrodeoxygenation (HDO) is a promising upgrading process for converting fast pyrolysis-produced bio-oil into petroleum-like hydrocarbon fuels or chemical building blocks. The creation of water removes the oxygen from the bio-oil [**72**].

Table 3 compares raw bio-oil to improved bio-oil produced through hydrogenation and catalytic cracking. Raw bio-oil has a lot of water, oxygen, and has a low heating value and hydrogen content, however, after utilizing these approaches all of these properties have improved.

Table 3. Bio-oil properties before and after catalytic upgrading [72].

Properties	Bio-oil	Hydrogenation	Zeolite cracking
Water content	15-30	1.5	-
HHV (MJ/KG)	16-19	42-45	21-36
Oxygen content	28-40	<5	13-24
Hydrogen content	5-7	10-14	2-8
Ph	2.8-3.8	5.8	-

Catalytic cracking

It is a suitable approach for enhancing bio-oil quality; it can reduce viscosity and density, enhance heating value, remove water content, and prevent phase separation. It is also a useful way to lower the O_2 concentration in bio-oil. For the reduction and conversion of higher hydrocarbons to lower hydrocarbons, it is commonly used in bio-refineries. The best option is the operating conditions for the catalytic cracking process are 400℃, 15 minutes of reaction time and a catalyst weight of 30 g, which results in the highest yield of petrol fraction obtained, which is 91.67g. The zeolite ZSM-5 catalyst is a potential catalyst for the catalytic cracking process of converting bio-oil to petrol [**73**]. Bio-oil can be created using pyrolysis. However, this product needs to be enhanced through a catalytic cracking procedure in order to be used as a transportation fuel. The catalyst is essential to the catalytic cracking process. This investigation's goal is to determine how catalysts (Ni and Si-Al) affect the upgrading of bio-oil [**74**]. Fast pyrolysis studies were performed in a fluidized bed reactor with a mixture of biomass and waste plastic at temperatures ranging from 525 to 675 °C. The experiment was completed by the authors at a temperature of 625 °C, with a maximum bio-oil output of 57.6%. It was discovered that the co-pyrolyzed bio-oil generated was of high quality [**75**]. During catalytic cracking, the majority of the oxygen in bio-oil was removed as water, with the remaining oxygen collected as phenolic compounds in the liquid result. The most remarkable finding of this study was the effective upgrading of bio-oil utilizing the co-fed method, which involved feeding 10% and 20% bio-oil into the fluid catalytic cracking reactor while maintaining the solvent (gas-oil) flow rate at 150 Kg/h. This method of upgrading bio-oil is used both with and without hydro de-oxygenation [**76**].

Catalytic cracking is used to upgrade bio-oil, and numerous reactions have been documented for both, including cracking, decarboxylation, decarboxylation, hydro deoxygenation, hydrocracking, polymerization, and hydrogenation. Hydro-deoxygenation and zeolite cracking occur due to the large diversity of chemicals in bio-oil [**77**].

Table 4. Physical properties comparison of the organic liquid and the raw bio-oil [78].

Property	Bio-oil	Organic liquid from Catalytic cracking	Organic liquid from non-catalyst cracking
Density (g/cm^3)	1.14	1.02	1.03
Kinetic viscosity (mm2 /s@50 °C)	12.7	4.72	4.85
Water content (%)	8.3	8.0	8.2
Cetane index	<20	39.76	38.18
HHV (MJ/kg)	23.1	31.8	29.9

Hydro-treating

Pyrolysis is commonly recognized as the simplest and least expensive method of obtaining liquid oil (bio-oil) from biomass. Because it requires considerable upgrading, such as hydro-treating, to remove oxygen, add hydrogen, and rearrange the carbon backbone, bio-oil cannot be utilized to replace petroleum as a high-quality fuel. In bio-oil hydro-treating technology, however, bio-oil instability is a key challenge. Hydro-processing removes oxygen as water by using hydrogen as a catalyst. This is typically regarded as a distinct process from fast pyrolysis, and it can thus be recognized as a processing condition for the production of a number of products, including petroleum refinery feedstock [**79**]. Cheng *et. al.* published results from experiments conducted in a batch reactor at three different temperatures using the same catalyst, Pd/C (200℃, 250℃ and 300℃). High reaction temperatures, such as 250°C and 300°C, appeared to boost biofuel hydrocarbon concentration. At a temperature of 250℃, biofuels with the highest heating value, highest hydrocarbon content, and lowest water content were created. In general, the oxygen concentration was reduced from 48.78 weight percent to values ranging from 30.20 to 36.85 weight percent [**80**].

They found good results when they used high acidity and large pore size bio-oil, including an increase in pH value and HHV, as well as a decrease in viscosity and density of bio-oil upgraded utilizing hydro treatment catalyst PdSZr and hydrogen atmosphere [**81**]. The usage of hydrogen during the catalytic hydro-treatment reaction will contribute significantly to the process's variable cost. [**82**].

One of the upgrading processes is hydrocracking, which involves breaking down large molecular inputs into smaller, more valuable outputs. The method incorporates a two-stage reaction: catalytic cracking of high molecular weight compounds in the first phase, followed by catalytic cracking of low molecular weight compounds in the second, followed by hydrogenation of the broken molecules in the third stage [**83**].

PHYSICAL TREATMENT METHODS FOR UP-GRADATION OF BIO-OIL

Physical upgrading of bio-oil is done by different chemical methods such as-

Emulsification

Emulsification is a straightforward, low-cost and efficient physical technique for preparing bio-oils for use in diesel fuel blends. It was determined that adding more bio-oil to diesel successfully reduced NOx emissions [**84,85**]. Diesel emulsions and quick pyrolysis bio-oils derived from biomass for diesel engines [**86**]. Whether there are any drawbacks to using bio-oil (biomass pyrolysis oil) as a transportation fuel (e.g., low heating value, high corrosiveness, and high viscosity). In today's transportation fuel infrastructure, emulsifying bio-oil and diesel is a cost-effective and convenient way to use bio-oil. The addition of an emulsifying agent (emulsifier or surfactant) to two immiscible liquids of diesel and bio-oil is a vital stage in the emulsification process [**87**]. Researchers were able to combine biodiesel with bio-oil to form a stable emulsion that contained both substances. They also suggested that the ideal conditions for a stable emulsion were a surfactant quantity of 4% by volume, an initial bio-oil/biodiesel proportion of 4:6, a swirling intensity of 1200 rpm, a blending length of 15 minutes, and an emulsifying temperature of 30°C [**88,89**]. When researchers compared the viscosity, corrosivity and water content of emulsions to raw bio-oil, they found that all three were decreased. Generally, it has been shown that properties including acid number, viscosity, and water content are desirable. When compared to the bio-oil levels before the emulsification process upgraded the bio-oil. Using micro emulsification with biodiesel, or fatty acid methyl ester, the emulsification of several bio-oils derived from various sludge's, including sewage sludge, paper/pulp sludge, and abattoir sludge, was explored. The study found that the best micro emulsions were produced when the biodiesel/bio-oil ratio was 10 and the bio-oil concentration was greater than 8% [**90**]. This suggests that micro emulsification is a potential method for upgrading bio-oil. The blending of bio-oil with diesel can result in an emulsion with much better fuel characteristics, such as a higher heating value and lower viscosity [**91**]. The oxygen concentration of bio-oil is reduced by catalytic cracking to around half of its initial values, and found that the upgraded bio-oil was predominantly made up of phenolic compounds [**92**]. Bio-oil properties has been compared with diesel and biodiesel, which has been discussed below in **Table 5**.

Table 5. Comparison of diesel, biodiesel, bio-oil, and a bio-oil emulsion fuel properties [**93,94**].

Fuel Property	Diesel	Biodiesel (B100) [106]	Crude Bio-oil [107]	40 vol.% Bio-oil/Biodiesel Emulsion
Viscosity (mm^2/s) (@40°C)	1.2 – 4.1	1.9 – 6.0	19.0	5.2
Water content (vol.%)	0.05	0.05	15 to 35	0.46
HHV (MJ/kg)	45.3	41.43	15.3	35.8
Density (kg/m^3) @20°C	853	880	1200	895
Acid number (mg KOH/g)	N/A	0.50	79.23	14.01

Steam reforming

Hydrogen has considerable development and exploitation potential and is frequently used as a raw material in the chemical industry and as a green energy source. Hydrogen and synthesis gas can be made sustainably and with minimal impact on the environment by steam reforming bio-oil and model compounds. For steam reformation on bio-oils, the first separation of the water-soluble components is necessary, and the rare metal catalyst used is expensive and easily passivates. The current study's objective is to find methods that successfully increase catalyst activity and stability while lowering catalyst cost in the steam reforming method of producing hydrogen [**95-99**]. Because the quantity of these gaseous products produced during steam reforming depends on the choice of an adequate catalyst, it is also a crucial task. The kind and activity of the catalyst also play a role [**100**].

SUPERCRITICAL FLUIDS

A novel method that uses supercritical fluid to upgrade bio-oil from fast pyrolysis has attracted a lot of attention in recent years. This method takes advantage of the special and superior characteristics of supercritical reaction media, such as liquid-like density, faster heat and mass transfer rates, dissolving power, and gas-like viscosity and diffusivity. SCF can be used as a reaction environment to create bio-oils as well as an improved medium to transform bio-oils into ones with a significantly reduced viscosity and a high calorific content [**101**]. According to Xiu and Shahbaz's explanation, the upgrading strategy using SCF often performed well for improving quality and yield when a catalyst like minimal silicate, zeolite, bi-functional catalysts, and other materials was used [**102**]. Following an upgrade, the quality of bio-oil and their constituent parts were both significantly improved [**103**]. Bio-oil can undergo supercritical fluid treatment to improve its energy content while drastically reducing its viscosity, acid number, and heteroatom content [**104**].

OTHER UPGRADING METHODS

Bio-oil and diesel are similar to one another in many aspects. As a result, a turning point in the practical use of bio-oil has been reached with the graded refinement of bio-oil employing petrochemical technology. A technique based on the division of bio-oil into light oil that is water soluble and heavy oil that is insoluble. The water-soluble light oil was treated with hydrogen peroxide to cause the aldehydes to oxidize into acids prior to catalytic esterification with ethanol [**105**].

CONCLUSION

The composition of bio-oil is complex, containing a large number of organic oxygenated hydrocarbon molecules and water. The high oxygen content of bio-oils has a number of major drawbacks that limit their widespread application. The quality of bio-oil is insufficient for direct transport and must be improved before it can be used in a strong engine. A frequent limiting feature of bio-oils derived from the pyrolysis of biomass feedstock and biomass-based platform chemicals is their high oxygen concentration. Physical and chemical upgrading procedures such as hydro-cracking, hydro-treatment, hydro-deoxygenation, emulsification, catalytic cracking, supercritical fluid and esterification can be used to remove this oxygen. All of these approaches can improve the quality of bio-oil by lowering its oxygen concentration and viscosity and they may be effective for commercializing bio-oil to the advantage of biofuel firms and the environment.

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