Review Article

# A Comprehensive Study on Bio-oil Production from Crude Glycerol

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**ABSTRACT**

Biomass is known as a promising alternative source to replace petroleum fuels due to the depletion of fossil fuels and an increase in fuel consumption. Biomass may be used for producing biofuels that are solid, liquid and gaseous. Liquid biofuel is more advantageous in terms of transport, storage, and high energy density than solid biofuel. Bio-oil, a liquid biofuel produced by various thermochemical techniques. This paper reviews the conversion of bio-oil using hydrothermal liquefaction and pyrolysis methods and the yield and properties of the bio-oil made from different biomass feedstock. Oleaginous microorganism makes use of crude glycerol for microbial conversion. Upgrading techniques are used to modify the unwanted properties of bio-oil for direct transport utilization.

**Keywords:** Bio-oil, Biomass, Thermochemical techniques-Pyrolysis, Hydro thermal liquefaction, upgradation.

## INTRODUCTION

In recent years, due to the depletion of non-renewable sources (fossil fuels) and to overcome the energy crisis, people focused on alternative energy. In addition, the usage of fossil fuels leads to the increase of pollutants and greenhouse gases such as sulfur oxides (SOX), nitrogen oxides (NOX), and carbon oxides (COX) in the atmosphere[1]. Biofuels as a source of renewable energy derived from biomass (biological material from living organisms or organisms that have recently been living) [2]. Through the process of biochemical, thermochemical, physical and/or chemical processes biomass is converted to biogas, bio-oil, and biochar[3, 4]. Biofuel is seen as a promising alternative resource for transportation, heat and electricity generation, especially from non-edible oil feedstock as well as its potential to be a part of a sustainable energy mix in the future. Biofuels are classified based on the raw material and technology used for production. Biofuels of the first generation are derived from food and oil crops that include vegetable oil, rapeseed oil, sugarcane beet, sugar cane and animal fat[5]. Biofuels of second-generation are produced to address the disadvantages of first-generation biofuels. That is derived from non-edible portions of plants such as wood and agricultural residues and non-food crops[6].

Microalgae are referred to as biofuels of the third generation and are considered a potential source of inexhaustibility. This potential is due to their availability and the highest lipid content present in them[7]. In advance, biofuels are produced by biological conversion by the use of microorganisms (e.g. *Saccharomyces cerevisiae, Methanogenicarchaea*or *Pyrococcusfurious*) [8]. Liquid biofuels have more advantages in comparison with solid and gaseous biofuels, such as transportation, storage, and high energy density.

Bio-oil is free-flowing, dark brown, highly oxygenated organic liquid [9]. It is the liquid portion of the biomass pyrolysis product and it contains a great amount of water (~40) [10]. Bio-oil generates low emissions of nitrous oxide and sulfur dioxide compared to diesel and petrol and is therefore known as clean fuel[11]. Thermochemical processing technology will turn the biomass into bio-oil. This includes the decomposition of biomass by heating in an oxygen-free atmosphere in a very short time period (1s). Fast pyrolysis liquids are non-miscible with hydrocarbons. Other than pyrolysis, bio-oils are produced using fermentation, hydrolysis and physical/chemical extraction and conversion processes. The high content of water in the bio-oil leads to separation in phases. Unless a large quantity of polar solvents such as ethanol is added, separation of this process is irreversible[12]. The three main constituents' cellulose, hemicelluloses and lignin present in the biomass can be turned into a complex mixture of bio-oil through depolymerization and fragmentation reactions. It may be used as a burner fuel directly or upgraded to fuels transport[13].

## PHYSICAL AND CHEMICAL PROPERTIES OF BIO-OIL

Bio-oil contains water content, solid particles content, viscosity, density, pH and fraction of pyrolytic lignin which gives unique physical and chemical properties[10]. Bio-oil is totally different from normal petroleum fuels. It has low viscosity because of its high water content. The high water content will affect its heating value. The bio-oil water content should, therefore, be below 30% [1]. Compared to water or any oil derived from petroleum bio-oil is the heavier one. Some of its properties are changes with respect to time such as its viscosity increases and its volatility decreases with time[14]. Bio-oil as a liquid fuel it meets some necessary fuel specifications. There are homogeneity, stability, heating value, pH, water, flash point, solids, ash, viscosity, and lubricity.

## COMPOSITION OF BIO-OIL

Bio-oil composition depends on the composition and origin of the feed material, the temperature of the pyrolysis, residence time, heating levels, collection system, and storage conditions[15]. Bio-oil has almost the same elementary composition as the feedstock for biomass and therefore has high oxygen content which makes it different from petroleum oils[16, 17]. It also contains a large proportion of fatty acids, such as acetic and formic acids. Bio-oils contain approximately 35-40 wt. % of oxygen, 55-60 wt. % of carbon, an acidic pH, density close to 1.2 gcm3 and 15-60 wt. %, or more of water [1]. Bio-oil also contains tar or pyrolysis tar, wood resin or liquid coal, liquid smoke bio-oil wood distillates, pyrolysis oil pyrolysis acids[8].

## PRODUCTION OF BIO-OIL

There are essentially two different routes available for biofuel production from different biomass.

- Thermochemical route
- Biochemical route

Bio-oil is produced from the thermochemical route. The quality and yield of bio-oil production may be determined by the organic content present in the biomass [18].

### Thermochemical route

In this method, biomass may be converted into bio-oil in the presence or absence of oxygen. It is the high-temperature treatment process. This method can additionally be classified into three processes based on heating rate, temperature range, and oxygen requirement[1].pyrolysis[2], liquefaction [19].

## PYROLYSIS

Pyrolysis is a technique of thermochemical processing used to decompose the organic material at a temperature of about 350-700ºC lacking oxygen[20]. It is also one of the most common economical and promising technologies for the conversion of biomass into liquid biofuels. The pyrolysis process' main products are flame retardant gas, liquid pyrolysis oil, and solid charcoal. Through this pyrolysis process, depends upon the ash present in the raw material the yields of the pyrolysis products may be varied. The yield of bio-oil in the range of 60-75 wt%, a gas yield of 10-20%, and a yield of char in the range of 15-25% [21]. The fast pyrolysis process has some necessary features for the productions of liquid bio-fuel. There are: (1) heat and heat transfer rates are very high, (2) vapor residence times were short (3) the temperature-controlled was very careful (4) the char was removed from the reaction environment rapidly (5) pyrolysis vapors are cooled rapidly [22].

### Various biomass feedstock used in pyrolysis technique

#### *Sugar cane waste*

There are certain important requirements such as availability, price, transportation, the environmental and social impact that are needed for renewable sources to replace petroleum for energy production. Alonso-Pippo et al (2004) performed fast pyrolysis of sugarcane in a reactor with a fluidized bed and evaluating the energy ratio for the produced bio-oil. At the temperature of 400-500ºC and short residence time, they heat the biomass by this fast pyrolysis process to avoid the destruction of the polymeric chains and undesirable secondary reactions[23]. Jessi Osorio et al (2017) used sugar cane bagasse as biomass for the bio-oil production in a fluidized bed reactor by catalytic fast pyrolysis technique at the pilot plant scale. They reported that the presence of catalyst will decrease the oxygen content by increasing the carbon dioxide level in the bio-oil. The addition of catalyst in the process will increase the quality of the bio-oil. Based upon the desired products and oxygen compounds various catalysts have been added during the pyrolysis process. They use calcium oxide (CaO) as a catalyst in the fluidized bed reactors. The presence of CaO decreased the bio-oils oxygen content by 14% and bio-oil yields have declined by 17 wt% and also reduce the water content but increase the gas content[24].

#### *Rice husk*

Rice husk is also one of the major sources for pyrolysis because of its unique physical properties. Lu Qiang et al (2008) derived the bio-oil from rice husk using a 120 kg/h intermediate pyrolysis system. The bio-oil derived from the rice husk was then tested according to the fuel-specific fictions for its chemical and physical properties. These analysis results can be used for evaluating the rice husk of bio-oil fuel quality. The bio-oil yield was high (50 wt %) at the temperature of 475ºC[25]. Jon Alvarez et al (2014) produced bio-oil in a conical spouted bed reactor, using fast pyrolysis. They reported that the main advantages of using the CSBR are to produce a high yield of bio-oil (70 wt %) at 450ºC, high heat, and mass transfer rates and very short residence times[26]. WenfeiCai et al (2018) produced bio-oil from rice husk in a downdraft circulating fluidized bed reactor at 550ºC, using fast pyrolysis. They analyzed the properties of bio-oil and reported that all those tested properties are related to the standard pyrolysis liquid biofuels in ASTMD7544-12 for biofuels in Grade G but the bio-oil water content is slightly more than that of Grade G biofuels[27].

#### *Wood residues*

By using fast and intermediate pyrolysis, Torri et al (2016) produced bio-oil from the residues of the soft and hardwood forest industries. Also, they compared GC/qMS and fGC ×GC/TOFMS for the characterization of bio-oil and reported that phenols and ketones as superior compounds. From the wood biomass, fast pyrolysis can produce approximately 70% of the raw bio-oil which requires high temperature (500ºC) and short time of residence (~2s). The presence of high ash content in the hardwood will decrease the bio-oil yield compared with softwood[28].

***Coconut shell***

Cellulose, hemicellulose, and lignin used as a raw material in the pyrolysis of coconut shell oil were the main components of the coconut shells. Tanya Rout et al (2015) produced bio-oil from coconut shells by using pyrolysis in a batch reactor at 575ºC. The maximum yield of liquid obtained was 49.5%. Then the fuel properties are analyzed by chromatographic and spectroscopic techniques. They reported that the obtained liquid was used as the stable resources for valuable chemicals and utilized as an alternative fuel[29]. Gao et al (2016) proposed that factors affecting the bio-oil yield obtained by coconut shell pyrolysis. The maximum coconut shell oil was obtained at the temperature of 475º C and the rate of heating is 10ºC/min. They reported that higher temperature has resulted in a reduction in the yield of coconut shell oil. The main components of coconut-shell oil were compounds containing water, aromatic, phenol, acid, ketone and ether[30].

## HYDROTHERMAL LIQUEFACTION (HTL)

HTL is the thermochemical process it usually requires low temperature (300-400ºC) high residence time (0.2- 1hr) and high pressure (5–20 Mpa). In these conditions, the biomass is broken into small molecules unlike pyrolysis and other gasification methods, the HTL process does not require the drying of the feedstock. In HTL there are mainly three processes: depolymerization, decombination, and recombination[31].

### Various biomass feedstock used in HTL

***Rice husk***

Xing-Zhong Yuan (2013) produced bio-oil from the rice husk by hydrothermal liquefaction process using mixed solvent (ethanol-water). The mixed solvent showed a synergistic effect at a relatively lower temperature. The bio-oil yield was highest at the temperature of 533K. GC-MS analysis results showed the effect of ethanol-water ratio, the effect of reaction temperature, the effect of solid-liquid ratio and the solvent fill ratio. Finally, they concluded that the increase in the solid-liquid ratio resulted in the negative impact in the bio-oil production and the increase in the solvent filling ratio resulted in the improvement in the production of bio-oil[32].

***Wheat straw***

Wheat straw is lignocellulose biomass that is effectively converted into bio-oil by the HTL technique. Patil et al (2014) produced bio-oil from wheat straw in a continuously operated tubular reactor by using the HTL process in both water and water-alcohol mixtures (ethanol and isopropanol). Also, they use the Ru/H-Beta (heterogeneous) catalyst for increasing the HHV values of more than 30MJ/kg in the presence of hydrogen. At 300˚C and 100 bar water-alcohol mixture was found to be the most efficient and the bio-oil was high (30.4%) [33].

***Pinewood***

The bio-oil of the HTL pinewood was dark and viscous liquids with a similar appearance to crude petroleum or heavy tar. Woody biomass has a high content of moisture and low energy density values. The conventional thermochemical process like pyrolysis and carbonization requires low moisture content. Mariusz et al (2019) produced bio-oil from pine wood by using batch autoclave HTL technique for the transformation of highly moisture biomass. The maximum bio-oil (38.35wt %) yield at 350ºC. Mid-infrared spectroscopy, gel permeation chromatography, GC-MS techniques are used to analyze the bio-oil chemical composition[34].

***Swine manure***

In the past thirty years, researchers have been investigated that the hydrothermal liquefaction process uses biomass having high lignin and high cellulose content (forest and agriculture residues) as a feedstock for liquid biofuel production. Xie et al (2010) produced bio-oil from the biomass having low lignin and low cellulose content using the HTL process. They use swine manure as biomass feedstock in a batch reactor at the temperature range of 260-340ºC, holding time 0-90mins and N2 pressure of 0-150psi. They reported that under the following conditions, temperature 340ºC, holding time 15mins and initial N2 pressure 150psi high yield of bio-oil were obtained. Then the GC-MS analysis method was used to study the composition and to classify the elemental compounds present in the bio-oil[35].

## MICROBIAL PRODUCTION OF BIO-OIL

Crude glycerol, a by-product of the processing of biodiesel contains a high amount of carbon source. 1kg of crude glycerol was produced from 10 kg of biodiesel. Crude glycerol contains different types of impurities such as oil, soap, fatty acids, and methanol depends upon biodiesel plant and catalyst used in biodiesel production. So, the delivery of crude glycerol causes many environmental problems[36]. A variety of microorganisms have the ability to utilize crude glycerol, as the carbon source for microbial oil production. Those organisms are known as oleaginous microorganisms that can grow in high carbon sources and low nitrogen sources[37]. Many organisms for example Yeast -*Yarrowia lipolytic* (36%)[38], Fungi-*Aspergillus oryzae* (57%)[39], algae- *Schizochytrium sp* (50-77%)[40], bacteria-*Arthrobacter sp* (>40%)[41] were found to be capable of utilizing the crude glycerol for the lipid production.

## UPGRADATION OF BIO-OIL

The raw bio-oil possesses certain unwanted properties including high acidity (TAN values 100-200), high water content, ash content, oxygen content, viscosity, and corrosiveness. In addition, bio-oil has low heating value, low volatility and quite unstable. These undesirable properties minimize the energy density within the bio-oil and for the utilization of bio-oil as a transportation fuel, the up-gradation is essential[21]. There are various techniques are available in recent times for the up-gradation of bio-oil. Such as hydro treating, hydro cracking, supercritical fluids extraction, emulsification, esterification (solvent addition), chemical extraction, and steam reforming. Among all of these upgrading techniques esterification (solvent addition) is the most commonly used technique because of the low cost of certain solvents and their value-added effects on the properties of the oil [42, 43].

**Hydro treating**

In the refinery process, the addition of hydrogen is important for improving the quality of the bio-oil and also increases the hydrogen content in the petroleum products. This process is known as hydrogenation. Hydro treating is hydrogenation and non-destructive process used to enhance the quality of the product without disturbing the boiling range and simultaneous cracking at the temperature of 500˚C and requires high pressure of up to 200 bars. During this process, oxygen content in the bio-oil was eliminated by the catalyst's sulfide Co/Mo/$Al_2O_3$, NiMo/$Al_2O_3$. The main drawback of hydro treating is catalyst deactivation and metal deposition[43].

**Solvent addition**

Polar solvents like methanol and ethanol having high heating values were added to the bio-oil will help to reduce the viscosity and enhance the quality and stability of the bio-oil. The following three pathways will help to reduce the bio-oils viscosity. (1)Actual physical dilution without the chemical reaction levels being impaired; (2) Reduced reaction rate by chemical dilution or oil microstructure modification; (3) chemical compounds interactions between the oil elements and solvent[43].

**Emulsification**

The pyrolysis oil is immiscible with hydrocarbon fuels but they are treated with surfactants then they can be emulsified with diesel oil. Jiang and Ellis use octanol as an emulsifier for stable bio-oil emulsion[44].

**Zeolite cracking**

zeolite cracking is ultimately used to reject the oxygen as $CO_2$ and CO for aromatic hydrocarbon production. Usually, this process requires high temperature (>350˚C). The temperature increase would result in reduced oil yields and increased gas yields. Unlike hydro treating, zeolite cracking does not want external hydrogen absorption and it is done at atmospheric pressure and requires high residence time for sufficient deoxygenation[43].

## APPLICATIONS OF BIO-OIL

For generating heat and power in boilers, sterling engines, Gas Turbines, Diesel Engines bio-oil is used as an alternative energy source. For transportation fuel bio-oil have some undesired problems for example high viscosity, high volatility, high water content, high ash content, high oxygen content, and corrosiveness. So, the bio-oil must be upgraded as it used as a fuel for transports. Bio-oil has a variety of chemical compounds that are used to create different chemicals in various sectors. For example, in pharmaceutical and fertilizing industries preservatives and additives, in food industries flavoring agents are produced. Currently, by adding water to the bio-oil, some industries produce liquid smoke from the bio-oil[45].

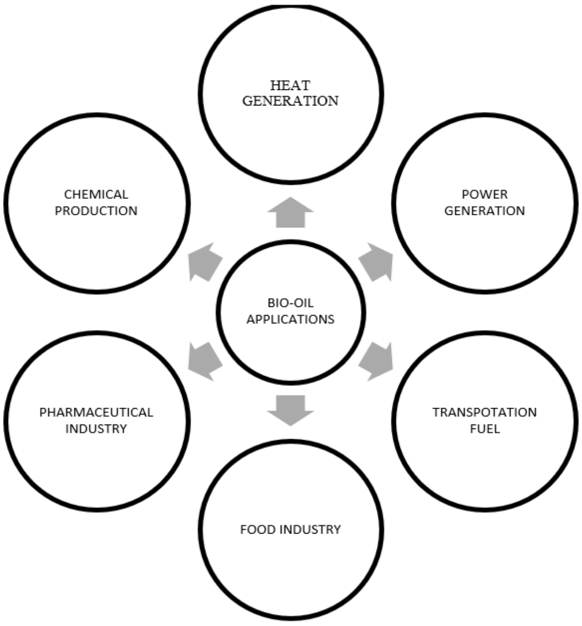


**Figure 1:** Applications of bio-oil

## CONCLUSION

It is necessary to choose the best way to convert the biomass into bio-oil as a valuable product. Mainly there are two processes used for the generation of bio-oil from various biomass feedstocks. In this paper properties and composition of bio-oil were discussed. Liquefaction and pyrolysis techniques used various types of biomass and different reactor and process conditions (temperature, residence time, pressure) to produce bio-oil. Compared to the liquefaction process pyrolysis method yield a high amount of bio-oil. Microbial bio-oil production is also a promising technique for the bio-oil production using various microorganisms. The produced bio-oil contains some undesirable properties which can impact the bio-oil for its transportation applications. Upgrading techniques are used to treat the bio-oil properties then it can be used directly as fuel for transportation.

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