



REVIEW OF BIO OIL UPGRADING FROM BIOMASS PYROLYSIS

Abdullahi, M. A¹, Garba, M. U², Eterigho E. J³, & Alhassan, M⁴
Chemical Engineering Department, Federal University of Technology, PMB 65
Minna, Niger State, Nigeria.

Corresponding author email: abdulmusavespa@gmail.com, +2348035312720

ABSTRACT

Pyrolysis is a promising method of converting biomass to renewable bio-oil. However, bio-oil is crude and its use in conventional engines is restricted without efficient procedure for upgrading. A critical literature review of the current status of production and bio oil upgrading from biomass pyrolysis is presented with the aim to identify new areas for further research. The technology of thermochemical process is described. The bio-oil is characterized by undesirable properties that affect its use. These properties need to be improved upon and this aspect is considered in terms of physical, chemical and catalytic upgrading. The increasing diversity of catalytic process, particularly the current trend of dehydrogenation and deoxygenation to eliminate coke formation and increase bio-oil yield was highlighted.

Keywords: *Biomass, Catalyst, Coke, Plastic, Pyrolysis.*

1 INTRODUCTION

Extensive consumption of fossil fuels (such as coal, petroleum, and natural gas) is predicted to grow steadily at the annual rate of 1.6% in the next two decades (Liu *et al.*, 2014.). These resources are recognized as a finite natural energy, because their current depleted rate is faster than their corresponding regeneration cycle. The massive utilization of fossil fuels results in the emissions of detrimental pollutants such as sulphur dioxide, oxides of nitrogen, and carbon dioxide which is responsible for triggering a sequence of environmental problems. Carbon dioxide as the main cause of global warming is emitted by means of burning fossil fuel. Renewable resources are receiving increasing attention as alternative to this depletion and environmental issues caused by the use of fossil resources (Aterny *et al.*, 2011).

Renewable resources are the natural sources that can be replenished after its consumption. It can be classified into sustainable (those that can be naturally renewable) and those that can be renewable with careful planning and harvesting. The most common examples of renewable resources are solar energy, wind power, tides, hydroelectricity and geothermal power. While biomass and biofuel are examples of renewable obtained after careful planning and harvesting.

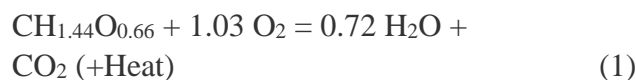
2 THERMOCHEMICAL CONVERSION PROCESSES

Thermochemical methods are more energy efficient and cost-effective (Leibbrandt *et al.*, 2011) compare to Biochemical conversions of biomass which is not cost-effective owing to the

fact that the biochemical techniques can solely take advantages of cellulose and hemicellulose in lignocellulosic biomass (Anex et al., 2010). These conversion technologies include torrefaction (between 200 -300° C), pyrolysis (350-600 °C), gasification (above 800 -1200 °C) and combustion (800- 1500°C). Combustion take place with sufficient air (oxygen) to completely oxidize the fuel for direct combustion or combined heat and power while gasification take place with insufficient oxygen or steam, so that complete oxidation does not take place. Pyrolysis takes place in the absence of oxygen or presence of inert gas to produce solid char, bio oil and bio- gas.

2.1 COMBUSTION

Combustion is a process of converting organic material such as biomass (woods, straw, bark residuals, sawdust, sawmills, switchgrass and so on) by means of burning to create heat and later, to generate power through steams. The conversion is essentially chemical reaction whereby biomass and oxygen are combined in high temperature environment to form water vapor and heat. The conversion can be briefly described as follows:



Note: $\text{CH}_{1.44}\text{O}_{0.66}$ is the approximate chemical equation for the combustible portion of biomass.

Though, the amount of heat produced during combustion of biomass varies depending on species, climate, and other factors, but it is generally about 20 Megajoules of energy per dry kilogram of biomass (Ciolkosz, 2014).

2.2. GASIFICATION

Gasification of biomass is a unique method that converts organic materials (carbon-based) in partial oxidation (not sufficient oxygen to allow for completely combustion) resulting in production of combustible gases consisting of Carbon monoxide, Hydrogen and traces of Methane. These gases when combined, producer

gas or syngas is formed through different steps of thermo-chemical reactions. The gas has a low-heating value fuel with a calorific value within the range of 4.2-5.02 MJ/ Nm³ (Reed *et al.*, 1982). The gas is usually used in internal combustion engines, for direct heat applications and production of chemical such as methanol.

2.3 PYROLYSIS

The advancement of thermochemical conversion of biomass is pyrolysis. Pyrolysis is thermal degradation of biomass that takes place at moderate temperature in which the biomass material is subjected to heat in the presence of inert gas (absence of oxygen). It is the fundamental reaction process that must proceed before the actual gasification and combustion of solid fuel occurs (Ralph, 2002). The thermal degradation of biomass in the absence of oxygen usually occurred at 400 – 600°C. The products of biomass pyrolysis include oils or tars, water, charcoal (or more correctly a carbonaceous solid), and permanent gases including methane, hydrogen, carbon monoxide, and carbon dioxide.

The process is carried out as slow or fast pyrolysis. Fast pyrolysis of biomass could obtain the highest mass yield (up to 80 wt% of dry feed) of liquid fuel and retain most energy (up to 70%) in the liquid products (Serrano *et al.*, 2011). Thus, the resultant fast pyrolysis oils have been viewed as the cheapest liquid biofuels and have attracted crucial attention at research over the past two decades. Furthermore, fast pyrolysis of biomass is on the verge of commercialization (Butler *et al.*, 2011).

2.4 BIO-OIL FROM PYROLYSIS OF BIOMASS

The products obtained from pyrolysis of biomass are char (carbonaceous solid), condensable gas (collected as oils or tars), and non-condensable gas (methane, hydrogen, carbon monoxide, and carbon dioxide). The nature of these changes depends on the heating rate of the material, the type of material undergoing pyrolysis and the pyrolysis temperature of the material. A typical

example of biomass materials includes wood, animal and plant wastes. The biomass materials are poor conductor of heat; therefore, it is important to manage the heating rate. The main biomass pyrolysis reaction is



Pyrolysis could be classified as slow pyrolysis, intermediate and fast depending on how the heating rate is managed. At high heating rate, more of non-condensable gases are produced while at low heating bio-char is the dominant product. At an intermediate heating rate, liquid bio-oil is the main product.

2.4.1 SLOW PYROLYSIS

Slow pyrolysis is also known as carbonization. It is performed at temperature range of 200-300°C or above 300°C residence time of 1 hour to several hours. It is referred to as torrefaction when it is carried out at a temperature range of 200-300°C, so that it results in near complete decomposition of its hemicellulose content in such a way that the mass and energy yield of solid product is maximized.

The main objective of torrefaction is to increase its carbon content thereby increasing the energy density of the biomass while decreasing its hydrogen and oxygen contents. The torrefied product offers clean burning fuel with little acid content in the smoke, lost in weight, high heating value and permits for use in pulverized coal fire boilers. The yields of products in carbonization are: 80% char and 20% gas, no water and organics. But when it is performed at higher temperature above 300°C, it produces more energy dense fuel with high energy yield. The yield of products obtained from carbonization includes 35% each of char and gas, 30% bio-oil (Bridgwater, 2012).

2.4.2 FAST PYROLYSIS

In fast pyrolysis, biomass decomposes quickly to produce more vapour, charcoal and gas. The vapour is rapidly cooled and a dark brown liquid is formed. Fast pyrolysis is carried out at temperature between 400 and 600°C, high heating rate (20 °C/min) and short residence time

(< 2 s) for vapours. Also, if the residence time of fast pyrolysis decreases, the liquid yield increases, and the yields of gas and char decrease. The yields of products in carbonization are: 80% bio-oil, 12% char and 13% gas (Bridgwater, 2012). Pyrolysis gas can be converted into fuel gas in the presence of oxygen and steam. Fuel gas is used as a fuel in Kiln, steam boiler, internal combustion engine and gas turbine.

Intermediate pyrolysis is carried out at temperature range of 400–500°C and has vapour residence time of about 10–30s. It is characterized with a low heat transfer rate which favours production of bio-oil with less tar. It is considered economical since the product is used directly as fuel engines. The yield of bio-char is 20–30%, gas 10–20%, and bio liquid of 50–60% for intermediate pyrolysis.

Figure 1 indicated the product distribution obtained from different modes of pyrolysis of woody biomass.

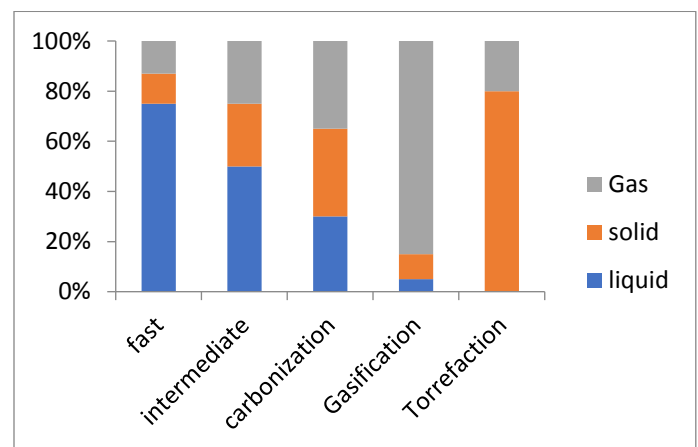


Figure 1: Mode of pyrolysis from wood biomass

2.5 PROPERTIES OF PYROLYSIS OILS FROM BIOMASS

The analysis and characteristics of bio oil qualities produced from biomass for various direct applications is very significant. The quality of any bio oil depends on its physical and chemical properties as well as the suitability of the oil for a specific function. The physical properties of bio oil include: viscosity, heating value, density, water content, oxygen content, pH



value, density and solid contents. While some of chemical compounds present in the bio-oil includes: various functional groups and their chemical bonding.

2.5.1 HEATING VALUE

The heating value is also known as the calorific value that ascertains the energy content present in oil (Bardalai, 2015). Calorific value can also be referred to as enthalpy of complete combustion of a fuel where all carbon and hydrogen are converted to CO₂ and H₂O respectively (Varmuza *et al.*, 2007). The calorific value of any oil can be considered as an important parameter for selection of the oil for a particular application. As the calorific value of oil increases, the oil can become more efficient and useful for different applications. The calorific value in most of the bio-oils are basically found within the range of 15- 36 MJ/kg which is always lower than the value of 40-50 MJ/kg for conventional petroleum fuels (Pattiya *et al.*, 2009).

The calorific value of a bio-oil mainly depends on factors such as water content, oxygen content, temperature and heating rate of the pyrolysis process. Normally, the presence of oxygen in significant amount increases the water content thereby reducing the amount of hydrocarbon (Mohanty *et al.*, 2011). Consequently, calorific value become affected and will not improve even if the bio oil undergoes any of upgrading methods. For example, eucalyptus wood, rice straw and waste bamboo have calorific value within the range of 16-19 MJ/kg, this value is much lower than the value of 40-50 MJ/kg for the conventional petroleum fuels despite the fact it undergoes upgrading (Kumar *et al.*, 2010).

Although, some of the various upgrading techniques that yields significant results through increasing the calorific value includes: hydrothermal pyrolysis, condensing at lower temperature and electrostatic precipitator (ESP). Hydrothermal pyrolysis is a good technique for upgrading bio oil quality, by using this technique, the calorific value increased up to 36-39 MJ/kg

which is much better than other pyrolysis oil (Xiu *et al.*, 2010).

Condensing the gases at lower temperature gives more improvement than at high temperature because, at high condensation temperature some of the gaseous elements having energy content are left out in the form of non-condensable gas (Yin *et al.*, 2013). Furthermore, reactor type does not have much influence on the quality of bio-oil upgrading in-order to improve the calorific value, for instance using auger reactor have the same results of calorific value range as compared with fluidised and/or fixed bed reactor (Ingram *et al.*, 2007).

2.5.2 WATER CONTENT

The water content in oil is often refers to as the amount of moisture present in the oil. The presence of moisture in high amount in bio oil can leads to separation of water (aqueous phase) and the heavier organic phase therefore, which make the application of bio-oil more difficult. Generally, the water content present in the pyrolysed oil from most of biomasses is found in the range of 10-40 wt. % (Bardalai, 2015).

Water content has negative influence on bio-oil these includes: low heating value of the oil, delay ignition, decreases adiabatic flame temperature which reduces the rate of combustion and causes injection difficulties during preheating (Lu *et al.*, 2009). The amount and variation of water content in the bio-oil completely depends on several factors, includes type of biomass, moisture content of the biomass, heating rate, temperature, vapour, residence time, rate of sweeping gas flow and so on (Heo *et al.*, 2010).

They are various methods that have been applied to reduce water content in bio oil. They include: solvent, condensation, hydro-deoxygenating, and electrostatic precipitator (ESP). Although the addition of solvent such as methanol can improve the flow quality of the oil, the water content increases. It has been demonstrated that condensation collected at lower temperatures shows a positive improvement of bio oil, for



instance condensation at -5°C contains less water content when compared to the condensation collected at 50°C (Asadullah *et al.*, 2007).

2.5.3 VISCOSITY

Viscosity of bio oil is the property that determines the characteristics of flow quality of bio liquid. The inherent bio oil viscosity obtained from biomasses does not depend largely on the type of reactor rather on other parameters. The parameters include: biomass feedstock, ageing of bio-oil, temperature, condensation, electrostatic precipitator (ESP) and water content (Bardalai *et al.*, 2015).

Biomass feedstock refers to smaller size of biomass and the smaller size gives high viscous oil. When bio-oil is kept or stored for certain period of time, its quality changes due to this ageing effect, the viscosity significantly increases continuously with the increase in duration of storage time because, during storage the volatile substance and the water present in the bio-oil get the opportunity to evaporate and thus the liquid becomes more viscous (Lu *et al.*, 2008).

Viscosity also increases by condensing the vapour at very lower temperature such as -5°C , again the effect of installation of electrostatic precipitator (ESP) is to improve the quality of bio-oil in terms of calorific value, but it seriously affected the viscosity, which make the viscosity increases to a very high value (Yin *et al.*, 2013). Hydrothermal pyrolysis gives high viscosity, for example in hydrothermal pyrolysis of swine manure; the viscosity is $0.843 \text{ N}\cdot\text{s m}^{-2}$ at temperature of 50°C .

Several methods or processes can be applied to reduce the viscosity of pyrolytic oil, for instance, addition of polar solvents like methanol or acetone reduces viscosity of pyrolytic oil but at the same time, it effects on some other properties also. The use of hot vapour filter is another technique for reduction of viscosity in the pyrolysis oil. Also, the amount of water content present in the bio-oil affects many properties, out of which the viscosity is one of them, such that

higher water content reduces the viscosity of the bio-oil very significantly. The effect of temperature occurred when temperature increases, the viscosity continuously reduces, for example viscosity of $0.0132 \text{ N}\cdot\text{s m}^{-2}$ measured at temperature of 40°C and continuously decreasing to $0.002 \text{ N}\cdot\text{s m}^{-2}$ when the temperature rose to 90°C .

2.5.4 ACIDITY

The acidity of bio-oils is usually determined as a numeric scale to specify oil concentration. While the pH of bio oil is hydrogen potential that measures the acidity from 0-14 as well as representation of the oil corrosiveness. The pH test method is useful for bio oil applications in which corrosive oil could cause significant damage. The bio-oils mostly contain organic acids such as acetic, carboxylic and formic acids. As the pH value of bio-oil becomes less, the oil becomes more acidic.

Because of the higher acidity, the bio-oil becomes corrosive and hence corrosion resistance material should be used in the bio-oil production and storage system. The pH value in the bio-oil depends on the type of biomass used for the bio-oil production. The pH of bio-oil is mostly within the range of 2-4 but few biomasses also have higher pH value (>4) such as rice straw, wheat straw and so on (Park *et al.*, 2004). On the other hand, some bio oil also have highly acidic properties as their pH value is found within 1.8-2.9, the typical example of the biomass is eucalyptus wood (Kumar *et al.*, 2010).

Some techniques have been established to increase the pH value of bio oil, fortunately a slight increase occurred, for instance, pH increased up to 4.5 by condensing the vapour at low temperature -5°C through the help of ice water mixed with a solution of sodium chloride (NaCl), instead of condensing at higher temperature $50-60^{\circ}\text{C}$ (Asadullah *et al.*, 2007). Again, when bio-oil shows two phases: top and bottom, generally it is seen that the top phase bio-oil have slightly higher pH value as compared to bottom phase.

2.5.5 DENSITY

The density of bio oil could be explained as the degree of compactness of a substance in a specific amount in the oil. The degree of compactness of a substance in the oil affects the energy value of the oil, for example, two different bio oils could have same heating value, may have different energy quantity as a result of variation in density. The density of bio-oil always decreases with increase in temperature and increases by condensing at low temperature (Garcia *et al.*, 2002).

Unlike other bio oil properties such as acidity, pH, heating value and so on, the density of bio oil is always found to remain the-same within some definite range of value for instance, the density 1100 kg/m³ remain same regardless of the installation of the hot vapour filter but, by using the ESP the density of the bio-oil could be increased to a higher value (Pattiya and Suttibak 2012).

Table 1 show the typical physical properties of bio oil include heating value, pH, viscosity, solid waste, density, water content, oxygen and ash content.

Table 1: Typical properties of wood pyrolysis bio oil.

Physical properties	Bio oil
pH	1.8-4.0
High Heating Value (HHV) MJ/Kg	15-36
Viscosity (at 50 ⁰ C) N·s m ⁻²	40-100
Solid wt. %	0.01-0.5
Density kg/m ³	1000-1300
Water content	10-40wt%
Oxygen	10-60wt%
Ash content	0.01-0.5

2.6 USES OF BIO OIL FROM BIOMASS

Application of bio oil refers to uses or conversion of bio oil to energy in various installed system specify as a form of technology such as power, heat, engine, turbine and so on (Asadullah *et al.*, 2007). Bio-oil product from fast pyrolysis of biomass has significant benefit: being a storable and transportable fuel. It is a potential source of energy, and a number of valuable chemicals that offer the attraction of much higher added value to industries than conventional fuels.

Bio oil from biomass can be considered basically carbon monoxide (CO) neutral and have a very little sulphur content compared to many fossil fuels. Bio-oil therefore, is a suitable substitute for heat and engine application than conventional fuel with an acceptable emissions level and is economically achievable. Currently, interesting applications for pyrolysis oil include: heat and power, automotive fuels, bio-refineries and chemical. At the moment, the applications of pyrolyzed oil are in varying stages of development, with only combined heat and power (CHP) having been demonstrated at a commercial scale (Meier, 2013).

The application and availability of Pyrolysis oil is becoming interesting and competitive in some part of the country in terms of the price of heating oil. In Europe and USA pyrolysis oil is not competitive because of the current low prices for natural gas. In contrast, countries like Brazil have high application and availability of biomass with low prices and a higher price for natural gas, pyrolysis oil seems to be competitive. In- some countries incentives are used to mandate transport system to use pyrolysis oil to replace natural gas (Muggen, 2015).

Pyrolysis oil can be used as substitutes to heavy and light fuel oils or natural gas in existing electricity plants. Substituting pyrolysis oil for fossil fuel is achievable by medium or large scale (co-) combustion with natural gas or heating oil fired boilers, furnaces and turbines to generate heat and power generation.



By direct combustion in a boiler or furnace, pyrolysis oil can be used to generate heat. This is the simplest and straight forward application of bio oil. However, various companies have been attracted for district heating to serve as substitutes for heavy fuel oil. One of the commercial companies is Red Arrow Products pyrolysis plant in Wisconsin, Canada frequently uses bio oil to generate heat for over 10 years (Freel *et al.*, 1996). Biomass technology Group (BTG) has demonstrated a successful test of co-combustion of pyrolysis oil in an industrial scale with natural gas-fired at a 350 MW power plant in Harculo, the Netherlands in 2003.

Gas turbines can be used to produce electricity and heat of CHP especially at remote locations. Currently, gas turbine has been adapted to run on pyrolysis oil to generate power, for example, Hengelo change from conventional fuel to run on pyrolysis oil to provide a 2MW class system of power generation.

In the world where biomass is available, pyrolysis oil can be made locally as well as used locally to produce power and heat. This is an added advantage where against some areas in the world where diesel and natural gas are still being used for diesel engines to produce power and heat. Another interesting application of bio oil is ship propulsion, in this field of application; pyrolysis oil is one of the little substitutes to fossil fuels that are commercially attractive. Also, pyrolysis oil has been tested successfully on stationary diesel engines.

Initially, second-generation fuels were not considered as automotive alternative fuels in transportation because of several problems such as poor volatility, high viscosity, coking, corrosiveness and high-water content. This second-generation bio oil can be derived from pyrolysis oil through different methods such as: direct upgrading, co-refining in existing oil refineries or through synthesis gas and subsequent synthesis processes such as methanol. Although, through upgrading bio oil can be used directly as transport. Also Chemicals such as

methanol, acetic acid, turpentine, tars, medical oil, furfural and so on can be obtained from pyrolysis of oil.

2.7 UPGRADING OF BIO-OIL

Currently, the following are inferior quality of bio-oils that make it very difficult for direct used as a transport fuel due to several disadvantages such as: high viscosity, acidic nature, low heating value, high water and oxygen. These disadvantages require upgrading physically, chemically and catalytically. In order to upgrade the fuel quality from bio-oil, a complete deoxygenation is required. There are different methods of bio oil upgrading:

2.7.1 UPGRADING OF BIO-OIL BY PHYSICAL

The following are the physical means of upgrading bio oil

- I. Filtration: using Hot-vapour filtration can decrease the ash content of the bio oil to less than 0.01%. Also, the alkali content can decrease to less than 10 ppm (Bridgwater, 2012).
- II. Solvent addition/esterification: The addition of solvents, particularly methanol, indicated a significant effect on the oil stability (Liu, 2014).
- III. Emulsification (emulsions): Pyrolysis oils are not properly miscible with hydrocarbon fuels but with support of surfactants can be emulsified with diesel oil (Ikura, 2003).
- IV. Distillation. This process is based on the different boiling point of every single component, the bio-oil can be divided into pseudo gasoline, pseudo diesel and pseudo aviation kerosene (Czernik, 2004).

2.7.2 UPGRADING OF BIO-OIL BY CHEMICAL

Currently, bio-oil has a relatively high-water content and high viscosity. Upgrading of bio-oil by chemical means is a good potential to improve



the quality by separating the bio-oil into value added chemical groups. Various approaches for upgrading bio oils into value added chemical products by means of extraction include: chemicals produced from the whole bio-oil, chemicals from fractionation of bio-oil, specific chemicals. The following are some potential approach of chemical extraction from bio oils:

Liquid-liquid extraction of bio oil is a technique of separating the value-added chemicals from bio oil based on their relative solubility of the oil and solvent; for example, separation of aromatics from bio oil via a water/chloroform extraction. Sugar derivatives in bio-oil can be successfully separated from aromatics via water/chloroform extraction. Based on this separation of aromatics from bio-oil, aromatics utilization in the bio-oil will serve as a great feedstock for fine chemicals or fuels.

Chemicals produced from the Whole Bio-oil: The entire bio-oil can be converted into valuable chemicals by taking advantage of its most available functional groups: carboxyl, phenolic and carbonyl. The functional group will be subjected to reaction in such a way that the non-reacting part of bio-oil would not have to be separated from the final product. For example, phenols and carboxylic acids can certainly react with lime to form calcium salts and phenates.

Chemicals from fractionation of bio-oil: Bio-oil can simply be separated into two fractions based on water solubility. The separation is done by simple addition of water into bio-oil, generally, a viscous oligomeric lignin-derived fraction settle down at the bottom while water soluble, mostly carbohydrate derived compounds is formed on top layer.

However, Bridgwater (1996) shown that, hydrotreating and zeolite-cracking are the best methods for upgrading bio-oil. Most of the experimental studies reported in the literature employed the use of fluid catalytic cracking catalyst such as zeolite and reforming catalyst such as transition metals supported on silica-

alumina (hydro-treating) for bio-oil upgrading of biomass. However, the zeolite catalysts have more advantage over reforming catalysts because of the former high selectivity and activity. Since the reviewed of bio-oil upgrading has been extensively discussed (Suchithra, 2012), only the more important features and current developments of catalytic cracking are reported here.

2.7.3 UPGRADING OF BIO-OIL BY CATALYTIC

Most of the experimental studies reported in the literature employed the use of fluid catalytic cracking catalyst such as zeolite and reforming catalyst such as transition metals supported on silica-alumina (hydro-treating) for bio-oil upgrading of biomass (Suchithra, 2012).

Hydro-treating of bio oil is the process of removing impurities of heteroatoms such as oxygen (Hydrodeoxygenation), where hydrogen react with oxygenated compounds under high pressure and mild temperature range of 350⁰C-500⁰C in the presence of heterogeneous catalyst to obtain water and hydrocarbon fuel. Hydro-treating is carried out in two steps; in the first step, the bio oil is treated at 250⁰C then followed by hydrogen reaction with oxygenated compounds at high pressure and high temperature to avoid polymerization reaction and coke formation. The second step involves hydrodeoxygenation (HDO) at high temperature and complete deoxygenation and the catalyst used for HDO process is sulphide CoMo or NiMo supported on Al₂O₃ (Milne et al., 1997).

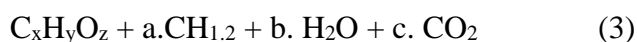
Though, hydrodeoxygenation of bio-oil has been shown technically possible but has some disadvantages. Some of the disadvantages are high coking (8–25%) causes catalyst deactivation and reactor clogging, poor quality of fuels obtained and economically not achievable (Milne, 1997).

Catalytic cracking: is the upgrading of bio oil in the presence of shape-selective catalyst such as



zeolites. However, catalytic cracking of bio oil is a process where oxygenated organics is converted into more valuable gasoline, olefinic gases, and other products oil in the presence of shape-selective catalyst such as zeolites (Bridgwater, 1996). Removal of oxygenated compounds via zeolite such as ZSM-5 occurred at atmospheric pressure and does not required hydrogen. ZSM-5 removes oxygen from bio oil as carbon dioxide and water.

Catalytic Cracking reactions of bio oil involve the separation of C-C bonds related with decarboxylation, decarbonylation and dehydration. In cracking reaction dehydration is the main reaction as shown in Equation 2.



During catalytic cracking of bio oil, the quality of bio oil normally improves and the upgraded bio-oil contained a reduced amount of oxygen but a high reduction in the oil yield is usually noticed (Oasmaa, 2003).

3 CURRENT TRENDS IN CATALYTIC CRACKING OF BIO OIL

Pyrolysis is an attractive method of converting biomass to transportation fuels (Kockar *et al.*, 2004) and (Asadullah *et al.*, 2007). Asadullah *et al.* (2007) reported that the conversion of bagasse to bio oil fuel in a fixed bed reactor at interval of 300-600°C. The analysis showed that, the yield of oil was very low (33.0 wt.%), low heating values of 19.91 MJ/kg, pH of 4.5. Although, Kockar *et al.* (2004) improved the yield by comparing the effect of fixed-bed of both slow and fast pyrolysis of rapeseed (*Brassica napus L.*) at 550°C, using two reactors, namely Heinze and tubular reactor. The results showed an increase in oil yields 51.7% and 68% that is (Heinze and tubular reactors) at different heating rate (30°C min⁻¹ and 300°C min⁻¹). Ala'a H. *et al.* (2016) reported that, due to strong acid activities of a catalyst with uniform pore size; pH increased, viscosity decrease and the heating

value increase up to 31.65 MJ/kg against 19.91 MJ/kg reported by Asadullah *et al.* (2007).

Jones *et al.* (2009) showed that bio-oil obtained from pyrolysis of biomass has chemical compositions which are similar to conventional fuels (gasoline and diesel fuels). But Huynh *et al.* (2012) compare bio oil to gasoline and diesel fuels properties and reported that, the bio oil obtained from biomass is of low quality. He confirmed the low quality by using rice husks and reported that the bio oil is lower than that of gasoline and diesel fuels.

Mohammed *et al.* (2014) also reported similar observation during the production of bio oil from castor shell and affirmed that, bio oil is also lower than that of gasoline and diesel fuels. Hence, it is paramount to upgrade bio oil from low quality to high quality to be of the same quality of gasoline and diesel fuels. In-order to upgrade the quality of bio oil catalyst is often employed.

Iliopoulou *et al.* (2012), Aysu *et al.* (2016) and Ala'a H *et al.* (2016) reported some findings on bio oil properties and upgrading as follows: Iliopoulou *et al.*, (2012) in their report compare the catalytic effect of silica sand, ZSM-5 (pure) and with that of ZSM-5 modified with nickel (Ni) and cobalt (Co). The bio oil produced from their experiment for silica sand was 58.67 wt. % (with oxygen 40.68 wt. %), ZSM-5 (pure) was 34.33 wt. % (with oxygen 4.24 wt. %) less in quantity but the quality was better. Similarly, Aysu *et al.* (2016), investigated the influence of catalyst during pyrolysis of lignocellulosic biomass in tubular and fixed bed reactor in the presence of these Ca(OH)₂, Na₂CO₃, ZnCl₂, Al₂O₃. Three catalysst showed good response of bio oil quality but less response using Ca(OH)₂. Therefore, they concluded that a better quality of bio oil was achieved but (34.05% of oil yield) less quantity of liquid (bio oil) and solid (bio-char).

Ala'a H. *et al.* (2016) compare the upgrading of bio oil in the presence of three catalysts: HY, H-mordenite and HZSM-5 in fixed fed reactor. The amount of liquid formed was high for HZSM-5

than HY and H-mordenite. This is because HZSM-5 has a strong acidity, uniform pore size and high activities. Their results showed that the quality of liquid increased, pH increased, viscosity decrease and calorific value increased up to 31.65 MJ/kg yet quantity decreases. Therefore, HZSM-5 catalyst can be considered as a potential catalyst to be used as direct fuel production. However, low bio oil yields and high coke that is being formed when catalyst is used which create the major problems against the effectiveness of using catalytic process (French *et al.*, 2009) and (Carlson *et al.*, 2009).

In recent times, biomass has been pyrolysed with plastics or alcohols in order to donate hydrogen to the biomass feedstock. This progression is testified to offer solution to the problems of less bio oil yield and the coke that is being formed. Çepeliog *et al.* (2013) reported their investigation of co-pyrolysis characteristics and kinetics of biomass-plastic blends of cotton stalk, hazelnut shell, sunflower residue, and arid land plant *Euphorbia rigida*, were blended in definite ratio (1:1, w/w) by using thermogravimetric analyzer (TGA). The analysis of kinetics showed an imperative pyrolysis mechanism and the yields of bio oil increased.

Onay *et al.* (2014) made a similar observation and confirmed that the synergetic effect during the pyrolysis of waste tire and non-food biomass at 500°C in the absence and presence of catalyst. In the presence of plastic, the analysis showed that the yield of bio oil increased. However, despite the fact that, plastic increase the quantity of bio oil but coke formation is a problem. Therefore, to reduce the coke formation, catalytic co-pyrolysis of biomass and plastics is required. In order to increase the quality, yield and reduce the coke, catalytic pyrolysis of biomass was co-fed with plastic or alcohol (Zhang *et al.*, 2016) and (Garba *et al.*, 2017). Zhang *et al.* (2016) studied the thermal degradation and kinetics of cellulose/ Douglas fir sawdust with plastics (LDPE) in present and absent of ZSM-5 catalyst by using thermogravimetric analyzer (TGA). The analysis of kinetics showed that addition of

catalyst does not alter the mechanism of decomposition. However, the quality and yield increases, consequently the coke reduced.

Recently, Garba *et al.* (2017) made a similar approach by comparing the pyrolysis of wood fuel using two different polyethylenes: low density polyethylene (LDPE) and high-density polyethylene (HDPE) over zeolite catalyst (ZSM-5) via a thermo-gravimetric analysis. It discovered that, the kinetics showed that the quality and yield of bio oil is increase when catalyst is co-fed with biomass and plastic.

4 CONCLUSION

This paper reviews the current trend on production and upgrading of bio-oil from biomass pyrolysis. Starting from production of bio oil from biomass, the paper shows progression in terms of quality and quantity when biomass is pyrolyse with catalysis and /plastic admixture. This progression is testified to offer solution to the problems of less bio oil yield and the coke formation.

REFERENCES

- Anex, R. P., Aden, A., Kazi, F. A., & Fortman, j. (2010). *Fuel. energy*, 89, 529-539.
- Asadullah M., Rahman, M.A., Ali, M.M., Rahman, M.S., & Motin, M.A. (2007). Production of bio-oil from fixed bed pyrolysis of bagasse. *fuel*, 86(16): 2514-2520.
- Aterny. J. C., & Serrano-Ruiz J. (2011). Dumesic for energy Environment. *Science*, 4, 83-99.
- Bardalai M. (2015). A review of physical properties of biomass pyrolysis oil. *International Journal of Renewable Energy Research (IJRER)*, 5(1): 277-286.



- Bridgwater A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *biomass and energy*, 68-90.
- Bridgwater, A. V. (2011). Review of fast pyrolysis of biomass and product upgrading. *ScienceDirect*, 80.
- Bridgwater, A. V. (1996). Thermal Biomass Conversion and Utilization. *Biomass Information System, in European Commission - Science, Research and Development*, 23.
- Butler, E. Devlin, G., Meier D., & Mc Donnel I. (2011). Renewable Sustainable Energy Rev. *green chemistry access*, 15, 4171-4186.
- Carlson, T. R. (2009). Aromatic Production from Catalytic Fast Pyrolysis of Biomass Derived Feedstocks. *Topics in Catalysis*, 52: p. 241 - 252.
- Cepeliog, O., & Ullar A. (2013). *Thermal and kinetic behaviors of biomass and plastic wastes*. Energy Conversion and Management.
- Ciolkosz, D. (2014). Introduction to biomass combustion. *wood energy*, 1. Retrieved from <http://articles.extension.org/pages/31758/introduction-to-biomass-combustion>.
- Czernik, S., & Bridgwater, A.V. (2004). *Overview of applications of biomass fast pyrolysis oil* (Vol. Vol.18). Energy & Fuels.
- Freel, B., & Graham (1996). Bio-Oil Production and Utilization . *Proceedings of the 2nd EU/Canada Workshop on Thermal Biomass Processing*, 23.
- Garba, M. U., Inalegwu A., & Musa, U. (2017). Thermogravimetric characteristic and kinetic of catalytic co-pyrolysis of biomass with low- and high-density polyethylenes. *Biomass Conv. Bioref*, 1, 4.8.
- Garcia-Pèrez, M. (2002). Vacuum pyrolysis of sugarcane bagasse. *Journal of Analytical and Applied Pyrolysis*, 65(2): 111-136.
- Heo, H., & park S. (2010). Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed. *Bioresourcetechnology*, 101(1): S91-S96.
- Ikura, M., & Stanculescu M., Hogan E. (2003). *Emulsification of pyrolysis derived bio-oil in Diesel fuel*. . Biomass Bioenergy.
- Ingram L., & Mohan (2007). Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. *Energy & Fuels*, 22(1): 614-625.
- Kockar, O., Onay, O., & Mete. (2004). Fixed-bed pyrolysis of rapeseed (*Brassica napus* L.). *biomass and energy*, 291.
- Kumar, G. P. (2010). Optimization of process for the production of bio-oil from eucalyptus wood. *Journal of Fuel Chemistry and Technology*, 38(2): 162-167.
- LeibbrandtN, H., Knoetze J. H., & Görgens, J. F. (2011). Biomass Bioenergy. *energy*, 35, 2117-2126.
- Liu R. H., Fei, W.T., & Shen, C. J. (2014). *Influence of acetone addition on the physio- chemical properties of bio-oils*. Energy Inst.



- Lu, Q., & Li. (2009). Overview of fuel properties of biomass fast pyrolysis oils. *Energy Conversion and Management*, 50(5): 1376-1383.
- Meier, D. (2013). state of the art of fast pyrolysis in IEA bionergy member countries. *renewable and sustainable energy review*, 20:619-641.
- Milne, T., Agblevor, F., Davis, M., Deutch, S., & Johnson, D. (1997). A review of the chemical composition of fast-pyrolysis oils from biomass. *Developments in thermochemical biomass conversion*, 409-424.
- Mohanty T., & Pant. (2011). Fuel production from biomass. *Indian perspective for pyrolysis oil*, 34.
- Muggen, G. (2015). Bio liquids fuel. *biomass conference*, 1. Retrieved from <https://www.btg-btl.com/en/application>.
- Oasmaa, A., Kuoppala, E., & Solantausta, Y. (2003). Fast Pyrolysis of Forestry Residue of Physicochemical Composition of Product Liquid. *Energy & Fuels*, 17: p. 433 - 443.
- Onay, O. (2014). The Catalytic Co-pyrolysis of Waste Tires and Pistachio Seeds. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 2.
- Park, Y., & Jeon. (2004). Bio-oil from rice straw by pyrolysis using fluidised bed and char removal system. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*, 49(2): 800.
- Pattiya, A., & Titiloye J.O. (2009). Fast pyrolysis of agricultural residues from cassava plantation for bio-oil production. *Carbon*, 51: 51.59.
- Ralph, P., & Overend. (2002). THERMOCHEMICAL CONVERSION OF BIOMASS. *National Renewable Energy Laboratory, Golden, Colorado, USA*, 1-5.
- Reed, T. B., Graboski, M., & Markson, M. (1982). The SERI High Pressure Oxygen Gasifier. *Solar Energy Research Institute, Golden, Colorado*, 234-1455.
- Serrano-Ruiz, J., & Dumesic, C. A. (2011). *Energy Environ. Sci.* 4, 83-99.
- Suchithra, T. G. (2012). Bio-oil Production through Fast Pyrolysis and Upgrading to “Green” Transportation Fuels. *PhD Thesis*, 35-56.
- Varmuza, K., & Liebmann. (2007). Evaluation of the heating value of biomass fuel from elemental composition and infrared data. *energy fuel*, 123.
- Wang, H. Jonathan M., & Yong Wang (2013). *Recent Advances in Hydrotreating of Pyrolysis Bio-Oil and Its Oxygen-Containing Model Compounds*. America Chemical Society.
- Yin, R., & liu. (2013). Characterization of bio-oil and bio-char obtained from sweet sorghum bagasse fast pyrolysis with fractional condensers. 1. *Fue*, 112: 96-104.
- Zhange, L. & Xuesong, J. (2016). *Catalytic co-pyrolysis of lignocellulosic biomass with polymers: a critical review*. *energy resources*.



**2nd International Engineering Conference (IEC 2017)
Federal University of Technology, Minna, Nigeria**



Zhu, X., Mallinson, R.G., & Resasco D.E. (2010). Role of Transalkylation Reactions in the Conversion of Anisole over HZSM-5. *Applied Catalysis A: General*, 379(1–2): p172-181.