Effects of Varying Pyrolysis Temperature on the Composition of Bio-Oil from *Parkia Biglobosa* Fruit Husk

Egga, E.S*., Ekwenchi,M.M., Enoh,B. S., Kangpe,N.S. And Yakubu,S.A. Department of Chemistry, University of Jos,P.M.B 2084, Jos Plateau State, Nigeria E-mail of corresponding Author: samegga13@gmail.com

Abstract

Moderate temperature decomposition of lignocelluloses from *Parkia biglobosa* fruit husk has been conducted to determine the effects of temperature on the composition of bio-oil. The result of proximate analysis shows that the ash, volatile, moisture and fixed carbon were found to be 3.12, 90.58, 3.32 and 2.98% respectively. The functional groups and chemicals compositions present in the bio-oil obtained for the three temperatures (200 $^{\circ}$ C, 250 $^{\circ}$ C,300 $^{\circ}$ C) were identified by GC/MS analysis. They are mainly alcohols, carboxylic acid, esters, ketones, with ethers and aromatic hydrocarbons which are valuable products for fuel and chemical industries. In addition, we can conclude that temperature influences the quantity and composition of bio-oil. The study shows that the bio-oil characteristics of *Parkia biglobosa* fruit husk is comparable with oils from other types of biomass thus, making it another potential source of fuel and chemicals.

Keywords: Biomass, Pyrolysis, bio-oil, Parkia biglobosa

INTRODUCTION:

Biomass is a renewable raw material which can be used for heat and fuel production. Solid biomass properties can be improved for example by pelletization, but converting them to liquid may further expand their utilization. Liquid bio fuels are easier to store, transport and handle than solid biomass (Solantausta and Oasmaa, 2003).

Globally, 140 billion metric tons of biomass is generated every year from agriculture. This volume of biomass can be converted to an enormous amount of energy and raw materials (A biomass assessment and compendium of technologies project, UNEP, 2009).

Biomass is a renewable resource that causes problems when not in use. As a common practice, direct combustion or dumping of agricultural waste under favourable anaerobic fermentation results in air pollution thereby posing risks to human and ecological health. The challenge, therefore, is to convert biomass as a resource for energy and other productive uses.

Sambo (1995) estimated crop residues and waste produced annually in Nigeria to be 6.1 million tonnes of dry biomass. Most of the crop residues especially in the North East part of Nigeria are rice straw which has been regarded as waste and is usually burnt (Ngugen et al, 1993). Or abandoned on the farms to decompose without control thereby imposing environmental problems such as global warming(Miller, 1994).

Parkia biglobosa fruit husk are among the abundant crops residues (as agricultural wastes) in most farms and in some gardens, and most farmers dump it on the farmlands to decay aerobically to be used as green manure. Some farmers also burn them to ash, to supplement fertilizer. Some farmers used it in fishing which is an illegal practice, while in some places it is soak in water for some days and apply to newly construct local floor (made of sand and gravels) and fence to add strength(Egga, 2012).

The burning of agricultural waste generates gaseous pollutants in the atmosphere, and also causes the destruction of some useful micro-organisms in the soil. In addition, dumping of organic substrate under favourable anaerobic fermentation condition leads to the generation of methane gas in the atmosphere without control. This also causes a serious environmental hazards because methane gas is a greenhouse gas that remains in the atmosphere for considerable length of time as reported by EPA (1986, 2005).

The process of bio-oil production from sugarcane biomass through fast pyrolysis has been already investigated in developed countries. During the 80's the Waterloo university in Canada was engaged in researches on the process with Canadian companies such as Dynamotive and Ensyn(Alonso-Pippo et al,2004).

Via thermochemical processing like fast pyrolysis, biomass can be transformed into liquid bio-oil, which can be stored and used for different applications (Adisak et al, 2008)

Bio-oil is a kind of liquid fuel from biomass materials such as agricultural crops, algae biomass, municipal wastes, and agricultural and forest by-products via thermochemical processes (Dermibas, 2004).

Bio-oil is known to be viscous, acidic, and thermally unstable and contains high proportion of oxygenated compounds (Czernik and Bridgewater 2004)

The utilization of husks from *Parkia biglobosa* fruit for energy and feedstock purposes not only raises hope for diversification of our economy but can contribute to the enhancement of the standard of living of our people.

This paper presents the effects of temperature on the composition of bio-oil from *Parkia biglobosa* fruit husk.

EXPERIMENTATION

Parkia biglobosa fruit husk were collected from Gindiri, Mangu Local Government Area of Plateau State. Samples were crushed and ground to $> 180 \mu m$. samples were then ready for proximate analysis and pyrolysis. **Pyrolysis of Samples**

In this work, a system to conduct pyrolysis was developed locally by the equipment and maintenance centre (EMC) of the University of Jos. The experimental procedure for pyrolysis of sample made use of a tubular loop reactor into which a heater, thermal sensor and thermal regulator were incorporated. The reactor is connected to U-shaped tube for collection of liquid products and unto a measuring cylinder inverted in water bath for the collection of gaseous products. The system was switched on and heated to required temperature. A specific mass is weighed and poured into test tube, corked and inserted into the tubular loop, connected by means of rubber tubing's unto the measuring cylinder. When decomposition starts, the liquid products were collected in the U-shape tube while the gaseous products were collected in the measuring cylinder by downward displacement of water, which measures the volume of gaseous products collected.

The product of interest (bio-oil) for the three different temperatures (200 °C, 250 °C, and 300 °C) were analysed using GC/MS QP2010 plus, Shimadzu, Japan, provided by National Research Institute for Chemical Technology (NARICT), Zaria.

RESULTS AND DISCUSSION

Table 1: Proximate Analysis of Parkia biglobosa Fruit Husk

Components	Wt (%)	
Ash	3.12	
Volatile	90.58	
Moisture	3.32	
Fixed carbon	2.98	
Table 2: Properties of the Bio-oil fro	om <i>Parkia biglobosa</i> Fruit Husk	
Property	Description	
Colour	Dark-brown	
Refractive index	1.343	
Odour	Irritating	
Density	1048.13kgm ⁻³	
pH	1.64	
Viscosity	55.12 cP	

Table 3: Suggested Compounds Present in Bio-oil from *Parkia biglobosa* Fruit Husk based on GC/MS assignment.

S/N Retention time(min	Retention time(min)	Name of component	Temperature (°c)		
			200	250	300
1	3.392	Propanoic acid(Luprisol)		+	
2	3.517	Acetic acid, hydroxy-, ethyl ester	_	_	+
3	3.792	Propanoic acid, 2-Hydroxyl-, methyl ester	_	+	
4	5.750	4-Methyl – 2, 4-bis(4- trimethylsilyloxyphenyl) pent-1-ene	+	_	_
5	6.583	Dimethylbenzene	+		+
6	6.600	Dimethlybenzene		+	
7	6.942	2(3H) – Furanone, dihydro	-		+
8	9.758	Hydroxybenzene (phenol)	-	-	+
9	9.875	2-Ethenylfuran	-	+	
10	14.733	Benzenediol	_		+
11	18.825	Benzenetriol	-	—	+
12	42.825	Tetrahydropyran Z-10-dodenoate	-	+	
13	42.883	gamma-Sitosterol	+	-	-

Key

NOTE: Except for Dimethylbenzene no other compound is

present in more than one extract.

+ Present

- Absent

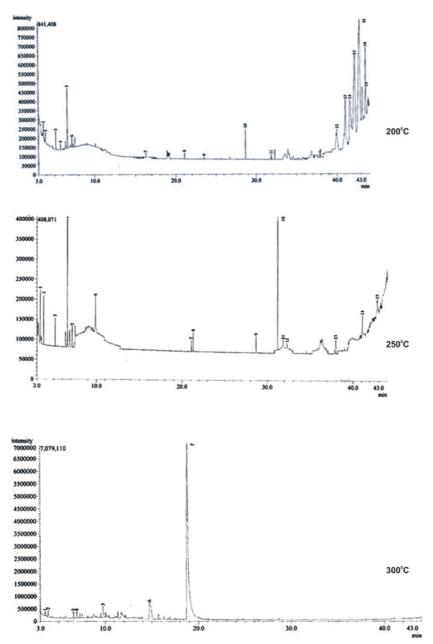


Figure 1: GC/MS Chromatograms for bio-oil from *Parkia biglobosa* fruit husk at 200, 250 and 300 ^oC respectively

Table 1 shows the percentage of ash (inorganic matter), volatile solids (organic matter), moisture and fixed carbon. The moisture content shows the amount of water absorbs and retains from the surroundings.

The ash content is usually related to the concentration of minerals present in the sample particularly for plant. The volatile solids indicate the level of organic matter that can be condensed into liquid.

The colour of the bio-oil was found to be dark brown. This agree with other literature reports that showed the appearance of bio-oil to vary from almost black or dark red – brown to dark green depending on the initial feedstock and the mode of pyrolysis (Dinesh *et al.*, 2006).

The bio-oil obtained has a viscosity of 55.12 cP. This value agrees with other literature values, that gives viscosity of bio-oil in the range of 25 - 1000 cP. Viscosity of bio-oil depends on the feedstock, the water content, the amount of light ends collected, the pyrolysis process used, and the extent to which the oil has aged (Dinesh *et al.*, 2006).

The refractive index of the bio-oil was found to be 1.343.

The odour of the bio-oil from *Parkia bioglobosa* fruit husk was found to have an irritating smell.

The pH of the bio-oil was found to be 1.64. This value differs from other literature values that give pH of bio-oil in the range of 2-4 (Czernik and Bridgwater, 2004). The decrease in pH is as a result of the presence

of acidic constituents in the bio-oil. This acidic nature has made bio-oil to be corrosive. This means that bio-oil fuel storage tanks will need careful materials selection; stainless steel and some olefin polymers that will not corrode due to acidic character of the fuel.

The bio-oil has a density of 1018.13Kg m⁻³ which is slightly lower than that reported by Dinesh *et al.*, (2006) as approximately 1200 kg m⁻³.

. Increase in pyrolysis temperature leads to increase of bio-oil yield.

Figure 1 shows that chromatograms of bio-oil for the three temperatures (200, 250 and 300 °C). The nature of the fractions formed evidently depends on temperature. The decrease in the number of peaks (number of compounds) with increasing temperature could be due to simultaneous depolymerization and fragmentation of lignocelluloses at higher temperature.

The three chromatograms shows different number of peaks with different retention times (RT) indicating the presence of different compounds on each. These compounds with different rentention time peaks were identified by the mass spectroscopy. The mass spectroscopy indicates the presence of alcohol, carboxylic acid, esters, ethers, ketones, and aromatic hydrocarbons in the *Parkia biglobosa* pyrolysis liquid. This result is found to be in agreement with the study of Czernik and Bridgwater (2004) on overview of applications of biomass fast pyrolysis oil. Most of the compounds identified using GC/MS included alcohols, carboxylic acids, phenols, esters, ketones, and aldehydes with ethers and aromatic.

CONCLUSION

The GC/MS analysis showed that the liquid composition was dominated by oxygenated species. The high oxygen content is reflected by the presence of mostly oxygenated fractions such as carboxyl and alcohol groups produced by pyrolysis of cellulose and phenolic acid and methoxy groups produced by pyrolysis of the lignin.

The bio-oil produced can serve as feedstock for production of various chemical products. These chemicals can be isolated, extracted and processed to meet customer specification.

In conclusion, the use of renewable biomass (*Parkia biglobosa* friut husk inclusive) feedstock would serves as potential source for a number of valuable chemicals.

REFERENCES

- Adisak P., James O. T. and Bridgwater A. V. (2008). Catalytic Pyrolysis of Cassava Rhizome. Bio-Energy Research Group, Chemical Engineering and Applied Chemistry, SEAS, Aston University, Birmingham, UK.
- Alanso-Pippo,W.,Rocha,J.D.,Mesa-Perez,J.M., Olivares-Gomez,E. and Cortez, L.A.B.(2004). In Ortega.E and Ulgiati,S.(editors) :Proceedings of IV Birnnial International Workshop "Advances in Energy Studies". Unicamp,Campinas,SP,Brazil. Pp 401-408.
- Czernik, S. and Bridgwater, A.V. (2004). Overview of Applications of Biomass fast pyrolysis oil. *Energy Fuels* 18, 590-598.
- Demirbas, A.(2004). Liquid fuels from agricultural residues via Pyrolysis, *Energy Sources*, 26, 281 827.
- Dinesh, M, Charles, U., Pittman, Jr. and Steele, P. H.(2006). Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels*, 20 (3) 848-889.
- Egga ,E.S.(2012).Moderate Temperature Decomposition of Lignocellulose from Parkia biglobosa fruit husks. MSc thesis submitted to the Department of Chemistry, University of Jos, Nigeria.
- EPA(Environmental Protection Agency).(1986). National air quality and emissions. Trends Report.1984 Research Triangle Park, NorthCalifornia. US Environmental Protection Agency,450/4,86-1001.
- EPA (Environmental Protection Agency)(2005)25-05-2005/US-EPA/methane EPA'Home/Global Warming Home: assessed 12/12/2005: http://www.epa.gov/methane.
- Miller, T.G.Jr. (1994) Living in the Environment. Wadsworth press, Belinont, California. Pp. 290-301.
- Nguyen,B.C.,Putaud, J.P.,Mchalophules,N. and Bonsang, B.(1994). CH₄ and CO Emissions from Rice Straw Burning in South East Asia. Environmental Monitoring and Assessment No. 31.Pp. 131-137.
- Solantausta, Y., and Oasmaa, A.(2003). Fast pyrolysis of forest residues and sawdust, production and fuel quality, *international Nordic bioenergy conference* Pp. 1-3.
- Sambo, A.S.(1995). Renewable Energy Technology in Nigeria, Resources Availability and Potential for Application to Agricultural: Journal of Agricultural Technology (JAT).Vol. 3,No. Pp1-25.
- UNEP (United Nations Environment Programme).(2009). Converting Waste Agricultural Biomass into A Resource, Compendium of Technologies. Osaka/Shiga,Japan.