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Pyrolysis of *Gmelina arborea* Wood for Bio-oil/Bio-char Production: Physical and Chemical Characterisation of Products

^{1,3}Edmund Okoroigwe, ²Zhenglong Li, ⁴Thomas Stuecken, ²Christopher Saffron and ³Samuel Onyegegbu
¹National Centre for Energy Research and Development, University of Nigeria, Nsukka. Enugu State, Nigeria
²Department of Biosystems and Agricultural Engineering, Michigan State University, East Lansing, USA
³Department of Mechanical Engineering, University of Nigeria, Nsukka. Enugu State, Nigeria
⁴Department of Mechanical Engineering, Michigan State University, East Lansing, USA

Abstract: *Gmelina* wood was pyrolysed in a bench scale screw pyrolysis reactor for bio-oil/bio-char production, at a reaction temperature of 454°C. The bio-oil and bio-char product yields were 71 and 13 wt.%, respectively while the rest accounted for wt.% of non-condensable gas and minor losses as feedstock dust. The products were characterized for physical and chemical properties to determine their potentials for energy use and industrial process applications. The results show that the bio-oil produced contains the major organic compounds typical of bio-oil from other energy crops used for commercial bio-oil production. The bio-char possesses heating value typical of pulverized coal, hence, it can be used as supplement to coal to reduce coal consumption in thermal power plants. The combustibility test of the flue gas produced blue flame showing complete combustion in excess of oxygen. This correlates with result of analysis of the gas contents using gas analyzer and GC/MS showing the presence of flammable gases such as alkanes, alkenes, hydrogen etc. Similarly, it compares relatively well with the results obtained with other woody biomass pyrolyzed in fluidized bed reactors.

Key words: Pyrolysis, bio-oil, *Gmelina*, bio-char, woody-biomass

INTRODUCTION

The search for global clean energy has led to the extensive screening of various biomass materials for alternative to fossil fuels as source of energy. Biomass is all embracing bio materials capable of releasing energy stored as a result of photosynthetic processes. These range from plant and animal materials to industrial wastes resulting from food and chemical processes. Biomass has been accepted to be future source of sustainable green energy because it contains less sulphur and nitrogen (Tsai *et al.*, 2006) which makes it environmentally friendly. One promising technique for biofuel production from biomass materials is fast pyrolysis. Fast pyrolysis is the thermal degradation of biomass materials in the absence of oxygen for the production of solid, liquid and gaseous fuels. The bio-oil product is a dark coloured viscous liquid with irritating smell. It has been successfully burned in boiler (Bridgwater, 1996; Boateng *et al.*, 2007), furnace (Bridgwater, 1996), engines and turbines for electricity generation as well as upgraded into transportation fuels (Boateng *et al.*, 2007). Fast pyrolysis is preferred to slow pyrolysis in that it favours the production of liquid

products and less of solid char and non condensable gases than the latter which maximizes the production of bio-char. The temperature of reaction is usually between 400 and 500°C while higher temperatures above 500°C and longer vapor residence time leads to secondary cracking of the primary liquid product thereby favouring production of secondary products such as gases. This also affects the quality of pyrolysis liquid produced. Fast pyrolysis of woody biomass is being studied in many places because of its promising future. The liquid product comprises of water, carboxylic acids, lignin-derived substances, aldehydes, ketones and carbohydrates (Oasmaa *et al.*, 2003, 2004) and such is different from petroleum fuel oils (Sipila *et al.*, 1998). Due to its chemical composition and physical properties such as high viscosity, density, instability at higher temperatures, high flash point etc the bio-oil undergoes upgrading for suitability as transportation fuel. Catalytic upgrading, hydrotreatment, esterification, cracking and blending with other liquid fuels are some upgrading techniques employed in improving the quality of the bio-oil. For instance, Oasmaa *et al.* (2004), improved the homogeneity and physical dilution of pyrolysis liquids by addition of

alcohol. This enhanced the solubility of the hydrophobic compounds which were high molecular mass lignin and extractives.

Many biomass materials of plant origin have been used for bio-oil production via thermochemical processes (Tsai *et al.*, 2006; Mohan *et al.*, 2006; Boateng *et al.*, 2007). Some of these are wastes from on farm activities (Pattiya *et al.*, 2008), wastes from forestry and wood industries (Oasmaa *et al.*, 2003) while some are from fast growing energy crops located in the temperate regions (Boateng *et al.*, 2007; Scott and Piskorz, 2009).

Gmelina arborea is one common tropical fast growing biomass that has not been extensively screened for bio-oil production. It is relatively abundant in Nigeria and some other tropical countries, where it is grown either in plantations or ornamentally in private and public places.

It can withstand dryness for 6-7 months, (http://www.hort.purdue.edu/newcrop/duke_energy/Gmelina_arborea.html) while it requires an annual rainfall of 750-5000 mm (Hossain, 1999). *Gmelina arborea* is a medium-sized deciduous tree up to 40 m tall and 140 cm in diameter (Jensen, 1995). In Nigeria, the yield of *Gmelina* is 84 m³ ha⁻¹ at age 12 in poor sandy soils, 210 m³ ha⁻¹ at age 12 in clay or lateritic soils and 252 m³ ha⁻¹ at age 10 in favorable alluvial soils—all volumes are under bark to 7.5 cm top diameter (Adegbehin *et al.*, 1988; Hossain, 1999). The wood specific gravity of *Gmelina* is given as 0.42-0.64 (Davidson, 1985). This implies that on favourable alluvial soils, the yield can be about 105.84-161.28 kg ha⁻¹ of wood at age 10.

Presently, in Nigeria *Gmelina* is commonly used for furniture making and as building materials for temporary wood structures as it is considered soft wood in building industry while in agronomy, it is considered a hard wood. This is because it belongs to deciduous plant family. It forms large percentage of wastes accruing from the wood industry in Nigeria because of its present use. This constitutes nuisance to the environment because the commonest way of disposing such wastes is by open burning or fuelwood as sawdust for domestic heating and cooking. Most times, open burning leads to environmental pollution due to emission of smoke, carbon dioxide and other green house gases. These however, are not without health deteriorating effects.

Better management of the wastes from wood industries utilizing *Gmelina* wood could be achieved by producing clean energy from the materials. The clean energy is derived from pyrolysis liquid serving as source of chemical energy (fuel) and useful industrial chemicals. This study is focused on characterization of the *Gmelina* wood as feedstock for bio-oil production, preliminary pyrolysis experiment for bio-oil and bio-char production and the characterization of the products.

MATERIALS AND METHODS

Feedstock: The feedstock was obtained and prepared at National Centre for Energy Research and Development, University of Nigeria, Nsukka. The wood sample was cut from mature *Gmelina* tree although its age was not known. It was air dried and ground to a particle size less than 1 mm passing mesh 40 (425 µm) using Wiley milling machine.

Feedstock and product characterization: The thermochemical characterization of the feedstock for proximate analysis (moisture, volatile and ash contents) were determined according to ASTM D3173-03, ASTM D3175-07, ASTM D3174-07, respectively while Fixed carbon was calculated as difference according to the relation: Fixed C = 100 - Ash (ar)-water content-volatiles (ar). The values were converted to dry and ash free (daf) basis using values of moisture content and ash. The elemental analysis for determination of Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur content of the solid sample and liquid product was carried out at Galbraith Labs Inc, Knoxville, Tennessee USA. Oxygen was determined using Thermo Finnigan Flash EA Elemental Analyzer. Sulphur was determined according to ASTM D4239-83, using LECO SC-432DR (Trace E16-2A) while Carbon, Hydrogen and Nitrogen of the feedstock material were determined by the LECO CHN 2000 analyzer. The ASTM D5373-02, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen and Nitrogen, Laboratory Samples of Coal and Coke was used for the analysis.

The bio-oil was analyzed for carbon and hydrogen content according to ASTM D5291-02, Standard Test Methods for Instrument Determination of Carbon and Hydrogen in Petroleum Products and Lubricants. While its moisture (water) content was determined by Karl Fischer (KF) titration method according to ASTM E203, Standard Test Method for Gross Calorific Value of Coal and Coke.

Heating values: The heating value is important parameter for measuring the energy value of samples. The heating value for the analysis sample was determined according to ASTM D5865, Standard Test Method for Gross Calorific Value of Coal and Coke on dry basis using the oven dried samples. The PAAR 1341 oxygen bomb calorimeter, standardized using benzoic acid pellets was used to determine the gross caloric value (HHV) while the net calorific value (LHV) was calculated using wt.% of hydrogen resulting from elemental analysis of the sample. The samples were pelletized using the Paar pellet press 2811. Ignition inside the bomb was in excess of oxygen at a pressure of 30 atm using 45 C10 fuse wire while the temperature of 2 kg of water surrounding the bomb was measured using the mercury thermometer.

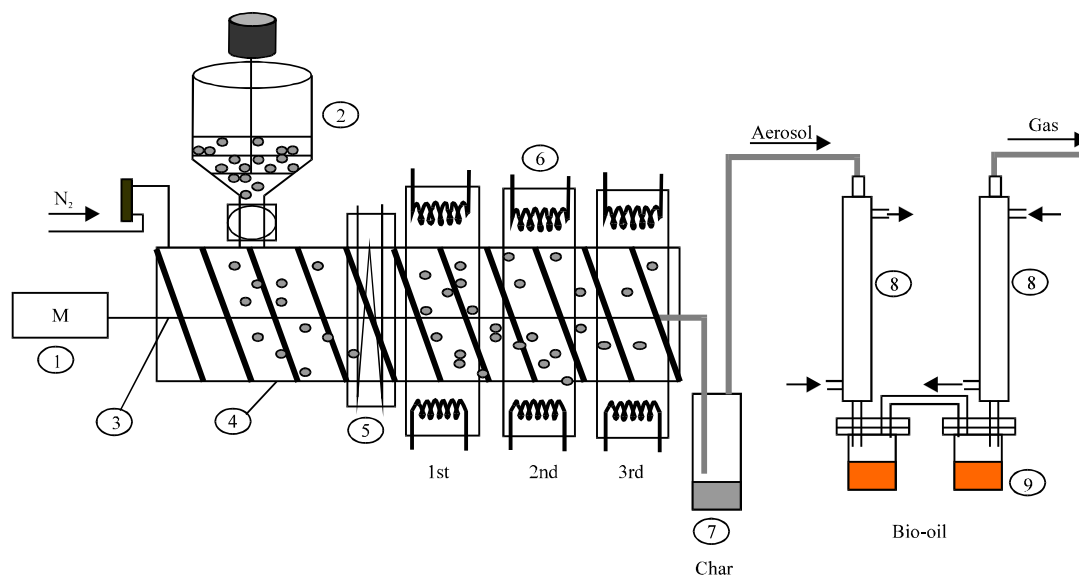


Fig. 1: Schematic diagram of the reactor used in the work. 1: Motor, 2: Biomass feed hopper, 3: Screw shaft, 4: Reactor barrel, 5: Feed cooling system, 6: Band heaters, 7: Char trap, 8: Bio-oil condensers and 9: Bio-oil containers

Structural carbohydrates and lignin: The composition helps in understanding its thermal behavior since, the cellulose and hemicellulose decompose at much lower temperature than the lignin. High lignin will lead to oil with much lignin derived water insoluble compounds which density is expected to be high also. These parameters were determined by two-step acid hydrolysis method as provided by NREL/MRI laboratory analytical procedure NREL/TP-510-42618 (Shuiter *et al.*, 2008). The sample was analyzed on as received basis using 72% sulphuric acid to breakdown all structural carbohydrates. The sugars in the hydrolysate were analyzed by high-performance liquid chromatography with refractive index detection (HPLC/RI) using D(+)-glucose, D(+)-xylose, D-cellobiose, L(+)-arabinose, D(+)-galactose and D(+)-mannose as calibration standards for determination of cellulose and hemicellulose components of the sample. The insoluble lignin was filtered using filtration crucibles and later ashed at 575°C. The acid soluble lignin was determined using Shimadzu UV spectrophotometer 1800 at a wavelength of 320 nm.

Pyrolysis experiment: Sample of *Gmelina arborea* wood was pyrolyzed using a bench scale screw reactor (Fig. 1) at temperature of 450°C. A total of 605 g of the sample was metered into the reaction chambers externally heated by 3 pairs of band heaters at 400, 430 and 450°C forming 3 reaction zones, respectively. Nitrogen gas was used as sweep gas to purge out oxygen in the system before and during the reaction. The hot vapour products produced were cooled to room temperature by a refrigeration system

using ethyl glycol solution at -24°C. The cooling (condensation) chambers are made of two vertical copper tubes. The first condenser uses water from melting ice flowing in counter direction with the hot vapour while the second condenser runs on the ethyl glycol. Most of the liquid products condensed at the first condenser while at much lower temperature further liquid product was collected in the second condenser. The non-condensable gases were let out of the chamber by gas delivery tube and collected into gas trap bags for analysis with gas analyzers. When tested for combustion, the flame was blue implying the presence of flammable gases confirmed to be H₂, C₂H₄, CH₄ by analysis of the gas. The pyrolysis products were analyzed using elemental, Karl-Fisher, thermal and spectroscopic methods to determine the potential of the products to be sources of renewable fuels and industrial raw materials.

RESULTS AND DISCUSSION

Physical characterization: The results are discussed in terms of the physical and chemical properties of the solid raw sample, the pyrolysis products and comparison to the products of other wood and agricultural residues previously used for bio-oil production. Table 1 shows the physical characterization of the *Gmelina* sample used in the analysis. It was air dried to a moisture content of 5.25% typical of that required for thermochemical analysis. The sample is a low ash material, with only about 1.37 wt.% on dry basis implying that the rest was available for conversion to energy. This possibly accounts for the

Table 1: Physical and chemical properties of the *Gmelina* wood

Property	Value		
	Ar	db	daf
Physical			
HHV (MJ kg ⁻¹)	21.24	22.36	22.67
LHV (MJ kg ⁻¹)	19.84	21.03	21.33
Proximate analysis			
Moisture content (%)	5.25		
FC	13.52	14.27	
Ash (%)	1.30	1.37	-
Volatile matter (%)	79.93	84.36	
Ultimate analysis			
C (%)	46.86		
H (%)	6.39		
N (%)	<0.5		
O (%)	44.84		
S (%)	<0.5		

ar: as received, db: dry basis and daf: dry and ash free. *Source Hossain (1999)

high volatile matter content 84.36% on dry basis. Similarly the low ash content implies low alkali metal content in the biomass. Biomass materials of high ash content do not make good sources of pyrolysis oil since, ash plays catalytic role in cracking of the liquid products to form gases (Nik-Azar *et al.*, 1997; Pattiya *et al.*, 2007) because of presence of alkali metal. The HHV and LHV of the sample are typical of wood samples used for pyrolysis. The values are lower than those of coal and higher than those of straw (Tsai *et al.*, 2006). The lower values are as a result of high oxygen content of the raw sample (Table 1). This is responsible for the oxygenated pyrolysis liquid product (Table 2) whose heating values are lower than those of fossil fuels.

The sample is a high carbon material as revealed by the elemental analysis while the low Nitrogen and Sulphur values position the sample as a source of bio-oil of low pollutant effect. The values of nitrogen and sulphur are, respectively lower than values for coal which contain 1.4 wt.% Nitrogen and 1.7 wt.% sulphur (Pattiya *et al.*, 2007). Hence, the biomass feedstock and its products are environmentally friendly source of bio-fuel.

The structural carbohydrate composition of the raw sample (Fig 2) shows that the sample is a low lignin material hence, the bio-oil is expected to contain less water insoluble heavy compounds but posses good thermal behaviour. The pyrolysis temperature should not be too high to avoid secondary cracking of the products. The sample composed of about 60 wt.% of cellulose and hemicelluloses which decompose at much lower temperature than the lignin (Mohan *et al.*, 2006).

The result of the bio-oil characterization is presented in Table 2. The crude bio-oil is red-brown and has pungent barbecue-like odour characteristic of bio-oil from woody biomass (Tsai *et al.*, 2006; Bridgwater *et al.*, 1999). The pyrolysis liquid product is composed of 26.42 wt.%

Table 2: *Gmelina arborea* bio-oil

Property	Value		
	Ar	db	daf
Physical			
KF moisture content (%)	26.42		
HHV (MJ kg ⁻¹)	17.62	23.94	24.07
LHV (MJ kg ⁻¹)	16.0	21.74	21.86
density (g cm ⁻³)	1.13		
Ash (%)	0.40	-	
Dynamic viscosity (cP)	54.5		
pH	2.55		
Ultimate analysis			
C (%)	41.47		
H (%)	7.42		
N (%)	0.72		
O (%)	47.77		
S (%)	<0.05		

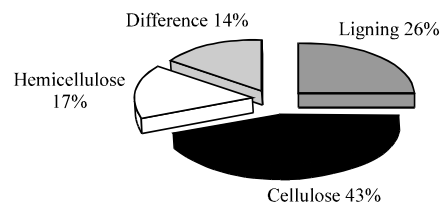


Fig. 2: Result of the compositional analysis of the wood sample

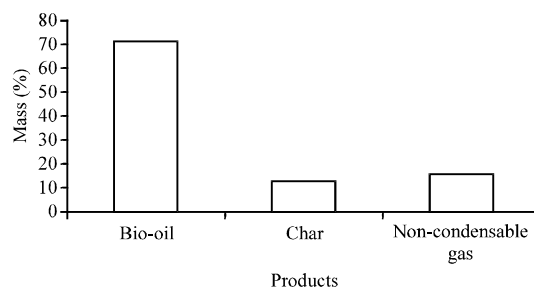


Fig. 3: Pyrolysis product yield percentage composition

moisture. This could be due to inherent moisture in the feedstock and water of dehydration reaction. The gross calorific values on wet and dry bases are lower than those of fossil fuels due to the oxygen content as explained above as well as for its high moisture content. These values however, are higher than those of pretreated and untreated pine wood reported by Hassan *et al.* (2009) even though its moisture content is higher. It is not certain if the location of the feedstock contributed in the quality of the bio-oil as regards its heating values. This may suggest that *Gmelina* may produce bio-oils of higher calorific values if produced from feedstock of very low water content. The LHV is higher than one half of that from fossil fuel. The liquid product ash content is typical of bio-oil from biomass materials.

The % product yield result of the pyrolysis experiment shown in Fig. 3 presents the major classes of

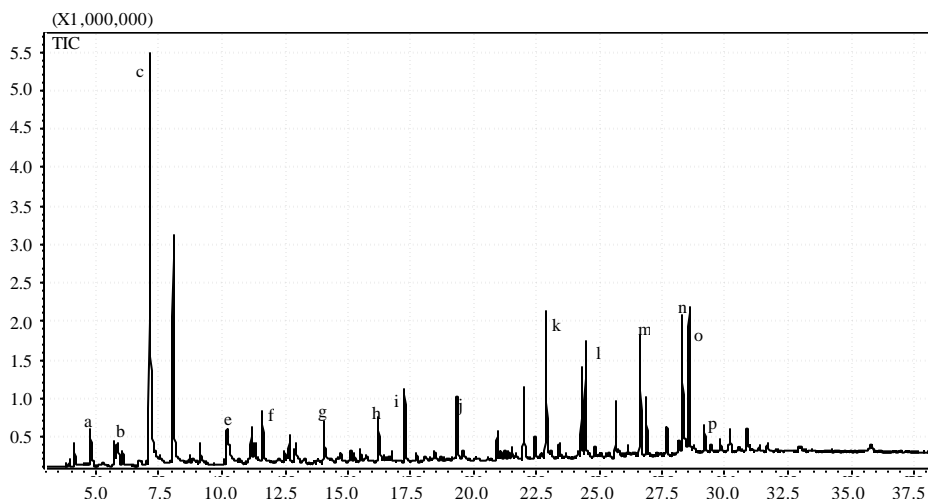


Fig. 4: Bio-oil chromatogram showing some major chemicals identified: a: Acetol, b: Dioxanediol, c: Acetic acid, d: Acetol, e: Ethyl pyruvate, f: 1H-Pyrazole, 3,5-dimethyl-, g: 6-Oxa-bicyclo[3.1.0]hexan-3-one, h: 1,2-Cyclopentanedione, i: Guaiacol, j: Phenol, or, 2-methoxy-4-methyl-, k: Phenol, 2,6-dimethoxy-, l: 1,2,4-Trimethoxybenzene, m: Phenol, 2,6-dimethoxy-4-(2-propenyl), n: 1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan), o: Phenol, 2,6-dimethoxy-4-(2-propenyl)-, p: Benzaldehyde, 4-hydroxy-3,5-dimethoxy

products formed which include 13 wt.% of biochar, 71 wt.% of pyrolysis crude oil and 16 wt.% non-condensable flammable gas. The result shows that under reactor and feedstock optimized conditions, higher yield of liquid product can be anticipated. The characterization of the solid product shows that the biochar HHV is 37 MJ kg^{-1} with 4 wt.% of ash on as received basis. Even though the percentage bio-char yield is relatively low, its energy content is higher than most coal species indicating that the product is a valuable source of energy. The bio-char can be utilized as source of energy for the heating of the reactor chamber.

The range of pH of typical wood-derived bio-oil is 2.5-3.4 (Ingram *et al.*, 2008). The pH of the pyrolytic liquid crude from *Gmelina* is 2.55 which falls within the range presented above from other woody biomass samples used in fast pyrolysis. This is because of the presence of organic acids - formic acid, carboxylic acids, acetic acids etc. (Tsai *et al.*, 2006; Czernik and Bridgwater, 2004; Bridgwater *et al.*, 1999) and alcohols as confirmed by Fig. 4. This implies that for engine and boiler applications, the bio-oil from *Gmelina arborea* should undergo upgrading to increase the pH to neutral level in order to prevent or reduce corrosive effects of bio-oil.

Chemical characterization of the bio-oil: The chemical characterization of the whole bio-oil from the bench scale reactor was analysed by dissolving 2 g of the oil in 10 mL methanol, after which the solution was analyzed using a

Shimadzu QP-5050A GC/MS. The GC used a Restek Rtx-1701 column, $60 \text{ m} \times 25 \mu\text{m}$ with a $0.25 \mu\text{m}$ film thickness. A split ratio of 1:100 was used to reduce the sample amount migrating through the column. Helium was used as the carrier gas at a column flow of 0.5 mL min^{-1} . The GC oven program was set to start at 40°C for 1 min and a heating rate of 4°C min^{-1} to 260°C . The injector and detector temperatures were set at 270°C . The mass spectrometer was operated in the Electron Ionization (EI) mode at ionization energy of 80 eV, m/z of 40-400 and a sampling interval of 0.34 sec. Identification of chromatographic peaks (Fig. 4) representing some of the chemicals was carried out by comparing the mass ions (m/z) of each peak with the 2005 NIST mass spectral database.

Figure 4 shows the chromatogram of the bio-oil when analyzed using GC/MS. Most of the chemicals have been identified by other scholars working with other biomass species (Pattiya *et al.*, 2007; Sipila *et al.*, 1998; Hassan *et al.*, 2009).

Char characterization: The solid product of the fast pyrolysis was characterized by determining its heating value and ash content. The Higher heating value was found to be 37 MJ kg^{-1} while its ash content is 4 wt.%. These values show that the bio-char can supplement coal in co-generation power plant for heat and electricity generation. It can also be a very good fuel in pyrolysis heating chambers.

CONCLUSION

Fast pyrolysis of *Gmelina arborea* wood was carried out and the products were characterized. The bio-oil yield of 71 wt.% is quite high when compared with yield from other energy crops such as switchgrass when pyrolyzed in a fluidized bed reactor. Thus under optimized condition of the reactor and particle size, higher yield can be expected. The bio-oil produced met the qualities of other liquid products from other energy classified woody biomass already screened for their potential source of bio-oil. The char possesses qualities comparable to coal which suggests that it could be a good supplement to coal in the bid to reduce coal consumption in power plants. Thus *Gmelina arborea* is a good biomass species for bio-oil and biochar production. When combined with the non condensable flue gas (NCG) product it can reduce the fossil fuel consumption in the pyrolysis industry for commercial bio-oil production. Hence, *Gmelina* is a good bio-energy source to meet the future renewable energy demand. When the fast pyrolysis equipment and processes are optimized, there is no doubt that it will contribute immensely to global renewable energy demand and assist in environmental protection.

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