

Experimental Investigation on the effect of Chemical Pretreatments of Slow-Pyrolyzed Nigerian *Jatropha curcas* L. Biomass Residues on Pyrolytic oil

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ABSTRACT

In Nigeria, assemblage and discarding of residues from energy crops are increasingly becoming laborious and costly and may pose serious environmental challenges if not correctly managed. The Energy Commission of Nigeria's long term (2016-2030) plan on the nation's energy requirements is entirely non-fossil. This is attributable to the global decline of fossil fuel sources, soaring prices, climate crisis and the need to utilize hitherto abundant biomass resources for energy and chemical feedstocks purposes in Nigeria. In this research, an experimental study on the bio-oil generated through slow pyrolysis of *Jatropha curcas* L. biomass residues – *Jatropha curcas* L. seed shell (JSS) and *Jatropha curcas* L. fruit hull (JFH) were realized in a fixed bed reactor at 450 °C in a batch-wise step, biomass sample (1.14 mm) particle size, designed by authors. The biomass samples were subjected to pretreatment with 4% sulphuric and sodium hydroxide solutions each respectively. The Chemical compositions and functional groups available in the bio-oil of both raw and pretreated biomasses obtained at 450 °C were investigated by Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform- Infrared (FT-IR) spectroscopy analysis respectively. Scanning Electron Microscopy (SEM) was used to look into the residual biomass surface morphology of pretreated and untreated *Jatropha curcas* L. waste of JSS and JFH. The results acquired disclosed that the bio-oil obtained from JSS and JFH might be a principal liquid fuel starting point and chemical feedstocks.

Keywords: Energy crops; Biomass resources; Slow pyrolysis; Chemical compositions; Functional groups; Bio-oil.

Introduction

The flourishing global biodiesel market has captivated investors and project developers in various countries of the world to contemplate biofuels production from self-sustaining non-edible biomass feedstocks. This is an attempt to lessen greenhouse gas emissions (which are

released during the combustion of fossil fuels) which contribute to global warming from fossil resources and reduce food versus energy issues. Furthermore, there are soaring energy requests all over the globe and consensus from researchers that fossil energy sources are limited. This makes it

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increasingly necessary to promote a renewable energy source of unlimited duration, little environmental impacts and which are technically achievable and widely available (Lateef *et al.*, 2014a; Lateef and Ogunsuyi, 2021). Biofuels synthesis from biomass is of interest because these biomasses are renewable, biodegradable, easily accessible and environment-friendly resources (Lateef *et al.*, 2018, Lateef and Asadu, 2018). *Jatropha curcas* L. is among the list of novel bioenergy crops in the regional potential appraisal carried out by Linde, 2012 in biofuel categories currently considered in fifteen ECOWAS countries (including Nigeria). *Jatropha curcas* L. (*Jatropha*) is a prominent multipurpose plant with many characteristics and appreciable potentials and are in abundance in Nigeria. The plant belongs to the family - Euphorbiaceae, which emanated in Central America, but is widespread in West and Central Africa countries (Abdul Khalid *et al.*, 2012; Lateef *et al.*, 2014b; Lateef *et al.*, 2014c; Lateef *et al.*, 2021). In Nigeria, the present focus of this prominent plant is largely on biodiesel (Lateef, 2010), the plant produces many other indisputably useful products (Openshaw, 2000; Manurung *et al.*, 2009; Parawira, 2010; Islam *et al.*, 2011; Abdul Khalil, 2013), but research efforts on valorisation is still at infancy in Nigeria. Currently, there is a wide abundance of *Jatropha* plants in Nigerian states of Kebbi, Kogi, Sokoto, Zamfara, Katsina, Kano, Jigawa, Bauchi, Yobe, Borno, Adamawa and Gombe (Galadima *et al.*, 2011). The oil derived from this plant find their uses in the production of soaps/detergents, cosmetics, biodiesels, insecticides, alkyd resins, transformer oil, biolubricants e.t. c.; nevertheless, the leftover from this plant- fruit hulls, husks or shells and de-oiled seed kernels are disposed of as waste.

There are many thermochemical procedures for the transformation of biomass into bioenergy or biofuels. The technique consists of gasification, pyrolysis, direct combustion/carbonization, transesterification, hydrocracking and biochemical

conversion technologies. Among the thermochemical conversion processes, pyrolysis is acknowledged as a favourable technology for bio-oil production (Ertas and Alma, 2010) and is considered as the technique by which fuels and chemicals can be produced from biomass materials (Capunitan and Capareda, 2013). Biomass pyrolysis is one of the known pathways for biomass conversion into bio-oil, which can partially replace fossil fuels, can lead to high added-value products and concurrently contribute to beneficiation of vast amounts of assembled waste biomass feedstock (Iliopoulou *et al.*, 2018). Pyrolysis is one of the identified simple conversion techniques to produce bioenergy from lignocellulosic biomass, energy crops and other biomass residues. Pyrolysis means thermal decomposition or cracking of biomass under a reduced oxygen environment or in an oxygen-free environment. Cellulose swiftly decomposes to gaseous products and residual char when biomass is treated at temperatures greater than 300 °C, because at lower temperatures, the decomposition is much slower and the products launched are less volatile (Kumar *et al.*, 2009).

There are three major pyrolysis paths for the conversion of biomass feedstocks to a wide variation of fuels and chemicals (Balat *et al.*, 2009). These are conventional pyrolysis, fast pyrolysis and flash pyrolysis. Conventional pyrolysis is described as pyrolysis, which occurs under a slow heating rate and is occasionally called slow pyrolysis. Compared to fast pyrolysis, the slow pyrolysis oil recovery is lower in mass yields but with lower oxygen and water content and better thermal stability (Elliot, 2007). Generally, Pyrolysis of biomass at high-temperature yields Charcoal (Carbon and ash called biochar), Condensable vapour (bio-oil / bio-crude, pyrolysis oil, pyrolytic oil), non-condensable gasses (CO, CO₂, Hydrogen) light molecular weight hydrocarbon gasses (-CH₄, syngas and producer gas). Bio-oil is the liquid condensate arising from vapours of a pyrolysis

reaction. Bio-oil is a dark brownish viscous liquid that bears some appearance to fossil crude oil (Sadaka and Boateng, 2009), and is viewed as a complex oxygenated compound comprising of water, water-soluble compounds, such as acids, esters e.t.c and water-insoluble compounds (usually called pyrolytic lignin). Generally, pyrolysis of biomass gives a complex mixture of products, its chromatographic analyses demand coupling of these instruments with a mass selective detector to assist the recognition of eluted products (Shah *et al.*, 2016b). These eluted products (condensate i.e Bio-oil) could be utilised as fuel when upgraded. It could also be harnessed for Wood preservation, Pesticides, Adhesives, Asphalt-paving substitution, Bio-carbon electrodes, Coal dust suppression, fertilizers, Antioxidants, Food additives, Impermeabilizer, Road de-icer and Surfactants (Murray *et al.*, 2014). For a better understanding of Bio-oil functional group compositional analysis, Fourier transforms infrared spectroscopy (FT-IR) is usually used.

Conversion of *Jatropha* plant parts into liquid biofuels such as Bio-oil involves three major unit operations: pretreatment, hydrolysis, pyrolysis. Pretreatment is necessary to boost the digestibility of lignocellulosic material (Hendriks and Zeeman, 2009). Pretreatment is necessary to depolymerize the complex lignin and cellulose structure and segregate lignin from cellulose and hemicellulose through hydrolysis (Den *et al.*, 2018). Pretreatment can also alter cellulose crystallinity, to magnify its depolymerization rate (Chundawat *et al.*, 2011). Hydrolysis requires impregnating the biomass in alkaline solutions and mixing it at a target temperature for a definite amount of time (Menon and Rao, 2012).

Biomass pretreatment can be categorized into four major classifications: physical, physicochemical, chemical and biological (Menon and Rao, 2012). Physical pretreatment involves mechanical processing for size reduction such as milling, chopping, pulverizing, irradiation (using gamma

rays, microwave etc) and extrusion to strengthen hydrolysis or biodegradability of lignocellulosic materials, which in turn lower the cellulose crystallinity. Physico-chemical pretreatments include steam explosion, ammonia fibre explosion (AFEX) / ammonia recycle percolation, Microwave-chemical pretreatment, liquid-hot water pretreatment. Chemical pretreatment consists of acid pretreatment, alkaline pretreatment, green solvents (ionic liquids). Biological pretreatment utilises wood degrading microorganisms, including white-, brown-, soft-rot fungi and bacteria to modify the chemical composition and/or structure of the lignocellulosic biomass. So far, there is no commercially realizable solution to effective pretreatment of *Jatropha curcas* L. biomass for the making of biobased products. Many pretreatment methods have been canvassed in the literature. Among these methods, mild alkaline and dilute acid pretreatments are more realistically useful due to fewer drawbacks when juxtaposed with others (Deng *et al.*, 2008). Keeping in view the significance of mild alkaline and dilute acid pretreatments, this study aims at the pretreatment of JSS and JFH with 4 % NaOH and H₂SO₄. Generally, as biomass is being pretreated, all the surface characteristics of the residual biomass change progressively.

Previous reports on pyrolysis of biomass wastes to bio-oil, biochar through flash / fast and slow pyrolysis have proved successful (Lee *et al.*, 2017; Ogunjobi and Lajide, 2013); to the best of our knowledge and the past work consulted so far, little or no work has been reported on the effect of pretreatments on chemical compositions, type of chemical groups present and residual biomass surface morphology of Nigerian JSS and JFH. Therefore, this work aimed to produce bio-oils from JSS and JFH using 4 % acid and alkaline hydrolysis, characterize the bio-oils for chemical compositions using GC-MS, verify the applicability of infrared spectroscopy (FT-IR) to gain fundamental knowledge of the type of

chemical group present and study the residual biomass surface morphology using Scanning electron microscopy (SEM).

Materials and Methods

Page | 4129 *Biomass sample and sample preparation*

The biomass samples used for this study were *Jatropha curcas* L. seed shell and fruit hull. The method used is as contained in our previous publications (Lateef *et al.*, 2021; Lateef and Ogunsuyi, 2021). Semi-dried *Jatropha curcas* L. fruits matured to a dark-brown state were picked manually in December 2017 from many *Jatropha* plantations located in Idah (7°05'00"N 6°45'00"E / 7.08333°N 6.75000°E), Kogi State, Nigeria. The *Jatropha* fruits were sorted separately to remove extraneous materials. The hulls of the fruits were separated from the seeds and were dried under the sun for 30 days. The dried hull was milled with a Grinding machine (SFE 200, 6.5 HP, Japan) and the pulverized sample were sieved through a laboratory test sieve (Standard test sieve, SETHI BSS 14, As per IS: 460 =1.41 mm) to ≤ 2 mm particle size. *Jatropha* husk (seed shell) were de-shelled manually by separating the kernels from the seeds. The seed shell was sun-dried for more than 30 days and milled in a Grinding machine (SFE 200, 6.5 HP, Japan) and then sieved (Standard test sieve, SETHI BSS 14, As per IS: 460 =1.14 mm) to ≤ 2 mm particle size. The leftover Kernels were milled in a Grinding machine (SFE 200, 6.5 HP, Japan).

The milled *Jatropha* fruit hull and seed shell were stored in perforated bags at room temperature (within a range of 26-32 °C) until used. All reagents used are of analytical grade and were used as received.



Fig 1: (i) *Jatropha curcas* L. seed shell (JSS) and (ii) *Jatropha curcas* L. fruit hull (JFH) biomasses

Proximate analysis of the raw feedstock and Higher Heating value

The initial moisture content of the samples was determined by the method of oven drying (Subroto *et al.*, 2015) modified, while that of Percentage ash was carried out based on AOAC, 1996 as follows:

Clean porcelain dishes were dried in an oven for about 30 min. at 105 °C, cooled at room temperature in a desiccator and weighed (w_1). About 1.000g (w_2) of the pulverized samples were then placed in the muffle furnace at 500 °C for 3 hours. The crucible containing the samples were allowed to cool in a desiccator and then weighed (w_3).

Percentage ash and fixed carbon of the biomass were estimated from equations 1 - 2

$$\% \text{ ash} = \frac{w_3 - w_2}{w_2} \times 100 \quad (1)$$

Percentage Volatile matter was determined based on Ibitoye, 2017 and that of Percentage Fixed carbon was computed by subtracting the total of moisture, volatile matter and ash percentage from 100:

$$\% \text{ fixed carbon} = 100 - (\% \text{ moisture} + \% \text{ volatile matter} + \% \text{ ash}) \quad (2)$$

The determination of Higher Heating/Calorific values was done using an e2k calorimeter (model: Cr1001).

A mass sample of 0.5g was weighed on the 2 cm firing cotton tied to the firing wire on the lid assembly and placed inside the metal crucible. The lid assembly was then placed inside the bomb (vessel) air-tight. The bomb was filled in with oxygen at 3000 MPa. The equipment was connected to a power source and the F1 on the keyboard attached to the e2k Calorimeter and the sample weighed (0.5g) were entered. The bomb Calorimeter was fired after placing the bomb inside it and the result was displayed on the screen after the combustion process. The bomb was removed and degas properly. The equipment was shut and the oxygen cylinder closed.

Wet chemical analyses (Compositional/ Fibre analysis which comprises Klason lignin, Hemicellulose and Cellulose) of *Jatropha curcas* L. waste biomasses were carried out according to the wood industry sector methods and as described in Carrier *et al.*, 2011 (modified) and the results published elsewhere

Pretreatment of *J. curcas* biomass feedstocks

J. curcas L. biomass feedstocks (JSS, JFH) pretreatment were carried out in a pilot-scale reactor designed by the authors. Biomass hydrolysis runs were carried out in a modified pressure pot with a continuous temperature control probe, where the temperature inside the vessel is maintained homogeneous. The treatment was performed on JSS, JFH at 120 °C, 30 min. residence time, with a different solid to liquid ratio.

Acid hydrolysis

In the pretreatment with dilute acid, biomass samples were soaked separately in 4 % sulphuric acid solution (Biomass liquid ratio was calculated in 1: 9; 500 g of biomass= 4500 mL of water) and subjected to heating at 109 °C for 30 min (Tutt *et al.*, 2012) modified. The pretreated biomass was

washed thoroughly with tap water, then 0.1 M sodium hydroxide was added to neutralize the acid, stirred thoroughly with tap water until neutral (pH adjusted to 7.0). The sieve was used to drain the supernatant from the residual biomass. The residual biomass was air-dried for 14 days and weighed. Air-dried residual biomass collected were subjected to further analysis and used for biofuel synthesis.

Alkaline hydrolysis

The alkaline pretreatment was carried out using 4 wt. % sodium hydroxide solution (Guilherme *et al.*, 2017) modified. The biomass feedstocks (JSS and JFH) were immersed in a 4 wt. % sodium hydroxide solution (Biomass liquid ratio was calculated in 1: 9; 500g of biomass= 4500 mL of water) and subjected to heating at 109 °C (followed by intermittent shaking) for 30 min. The pretreated biomass was washed thoroughly, then 0.005 M of H₂SO₄ was introduced to neutralize the base, stirred thoroughly with tap water until neutral (pH adjusted to 7.0). The sieve was used to drain the supernatant from the residual biomass. The residual biomass was air-dried for 14 days and weighed. Air-dried residual biomass collected were subjected to further analysis and used for biofuel synthesis.

Slow Pyrolysis of biomass feedstock

Pyrolysis reactor is of fixed bed type and made of Brass steel and cylindrical shape. The cylindrical reactor is having an internal diameter of 20 mm and height of 70 mm, which is placed in an electric furnace with a heating element of 1mm thickness. The electrical furnace is connected to the Electrotechnical system: temperature controller unit (Temperature controller, C900FK07-M*EN, 0-1300 °C, 220 V, AC 50/60Hz, Japan), Contactor (Cutler-Hammer, C316KNA3, Germany and a Sensor (Thermocouple, K -Type, China) which governs the inside temperature of the furnace and another temperature controller unit which governs the inside temperature of the reactor. To create an

oxygen-free environment, the reactor was neatly packed with a heat-resistant gasket. The temperature of the furnace was set at 450 °C and as the biomass sample (≤ 2 mm particle size, 1000 g) gets pyrolysed at about 245°C, volatiles released, exits from the volatile delivery tube and are passed through the Liebig condenser. The sample was pyrolysed to the set pyrolysis temperature of 450 °C and held for about 45-50 min. until no release gas was observed from the reactor. The pyrolysis liquid products - viscous phase (Bio-oil) and aqueous phase (water) were collected *via* flat bottom flask by condensing in the condenser and cold traps maintained at about 0-5 °C. The viscous phase was separated from the aqueous phase using a colloquially sep funnel, weighed and stored in a plastic container for further use and analysis. The biochar resulting from pyrolysis was equally weighed and stored inside a polythene bag.

Analytical methods

Bio-oil and pretreated residual biomass obtained were further analysed using the following analytical methods to obtain information on pyrolysis product / residual biomass characteristics.

Gas Chromatography-Mass Spectrometry (GC-MS) of the Bio-oil.

Extraction and cleaning up of the extracts

Five (5) mL of the sample was weighed into a beaker and 10 mL of hexane was added. The sample was sonicated for 10 min in an ultrasonic bath and the extract was transferred to another beaker. The extraction was repeated with 10 mL of the solvent mixture. The extracts were combined, concentrated to about 2.0 mL. Clean-up of the extract was done with a glass syringe loaded with silica gel, glass wool and anhydrous sodium sulphate and then eluted with 5 mL of hexane. The purified extracts were then reconstituted in 2 mL hexane.

The GC-MS was used to identify the chemical compositions of the bio-oil. The analysis was

executed using Agilent Technologies 7890 A equipped with 5975 MSD with HP-5ms capillary column (30 m length, 0.32 mm internal diameter, 0.25 μm thickness). Helium gas is used as carrier gas at a constant flow rate of 1 mL per min. The injection was achieved in spitless mode and the injector temperature was set at 250 °C. The oven temperature was programmed from 90 °C for 0 min, then at 3 °C per min to 180 °C for 10 min. Identification of the compounds was carried out by comparing the spectra data of the sample with reference spectra in spectra libraries (NIST).

Fourier Transform- Infrared (FT-IR) analysis of the Bio-oil

The surface chemical properties of the raw and hydrolysed (acid and alkali) Bio-oil achieved through slow pyrolysis at 450 °C were performed using an Alpha sample compartment RT-Dia TGS with serial number 104319. About 0.4 mL of the Bio-oil sample were smeared to cover the sample crystal. The absorption bands were obtained at 4 cm^{-1} with a 400-4000 cm^{-1} scan range. Spectra were collected in 40 sec. The data were compiled using OMNIC™ spectroscopy software displaying spectrum region, absolute threshold and sensitivity.

Scanning Electron Microscopy (SEM) analysis of raw and hydrolyzed samples

The morphological characteristics of raw (unmodified) and hydrolysed (modified) *Jatropha curcas* L. biomass used for Bio-oil production were studied by electron microscope (SEM, JSM-6390LV, 6733B-IUUS-SN, Thermo Electron Corporation, USA) adapted with an energy dispersive X-ray (EDX) Spectrometer and X-max detector (Oxford-instruments, INCA 400, UK). The samples were placed on the SEM stub using double-sided carbon tape, fitted into the chamber controlled at around 1.4×10^{-3} , 15 kV accelerating voltage, 5 – 100 μm working distances and 50-5,000 times magnification.

Results

Proximate Analyses

Proximate analysis of fuel or biomass gives the percentage of the materials that burn in a gaseous state (volatile matter), in the solid-state (fixed carbon), and the percentage of inorganic waste material (ash) and hence is of major significance for biomass energy use. Table 1 shows the results of JSS and JFH biomass proximate analyses. The physicochemical properties of the bio-oil are published elsewhere.

Characterization of the tested Biomass

The results obtained for the Proximate and Calorific (Heating) value of the tested biomass are shown in Table 1.

Table 1: Characterization of the tested (raw, untreated/ untorrefied) *Jatropha* waste Biomass

Analysis	Waste Biomass	
	JSS	JFH
Proximate analysis		
Moisture content	8.79	10.14
Ash content	4.99	16.50
Volatile matter (VM)	71.80	54.73
Fixed carbon (FC)	14.42	18.63
Calorific (heating) value (MJ/Kg)	17.37	13.80

The Ash, VM and FC are conducted on a dry and dry ash-free basis respectively. All analyses were conducted in duplicate and the values recorded are averages of two values.

Moisture content

The moisture content is a critical efficiency parameter because it hurts combustion processes thereby affects the calorific value of biomass material; it also interferes with transportation costs, storage and drying of the biomass (Rambo *et al.*, 2015).

The moisture content of JSS and JFH was relatively higher – 8.79 % and 10.14 % respectively, but are within the range accepted for biomass conversion to fuel use. Singh *et al.*, 2008

reported 10.75 %, 12.35 % for JSS and JFH respectively. According to Grover and Mishra (1996), Moisture content should be as low as possible, normally in the range of 10-15 percent for any potential agro-residues to be reasoned for thermochemical conversion. Generally, when the moisture content is low, the pellets or briquettes produced from the biomass will effortlessly be ignited and that no slagness during burning will occur (Akintaro *et al.*, 2017).

Ash Content

The ash content of biomass varies significantly. The ash content is a non-combustible constituent or matter after the ignition of biomass at a high temperature. From Table 1, the ash content of *J. curcas* L. waste was 4.99 % for JSS and 16.50 % for JFH respectively. The JSS ash content of 4.99 % is within the ash content of other agro residues: 4.2 %, 4.3 %, 4.6 %, 4.8 % for Tamarind husk, Coffee husk, Cotton shells, tannin waste and Almond shell respectively (Grover and Mishra, 1996). The ash content of 4.99 % for JSS in the present study was higher than values reported in some other studies, e.g. 4.00 % (Nahar and Ozores-Humpton, 2011). The JFH has an ash content of 16.50 %. The JFH biomass ash content is lower than 22.4 % for rice husk, 19.1 % for tobacco dust and 28.2 % for de-oiled bran (Grover and Mishra, 1996). The JFH ash content is higher than 14.88 % (Nahar and Ozores-Humpton, 2011). A high concentration of ashes might be a threat in the furnaces since there is a higher probability of ash deposition and slags, as well as corrosion of the surfaces of the furnace. The ash content of the biomass is an indicator of slagging behaviour of the biomass, therefore lower ash content of biomass feedstock is always desirable for biomass conversion. The JFH ash composition result reveals that it has a high ash content

Volatile Matter

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Volatile matter content is another essential parameter because it gives evidence of the reactivity and ease of ignition of organic material (Flores *et al.*, 2017.) The volatile matter for JSS and JFH is 71.80 % and 54.73 % respectively. Volatile matter is described as a solid material in fuel that when heated at a specific temperature, converts directly into a gaseous phase without undergoing a liquid phase (Acar and Ayanoglu, 2012). This means there is more solid content that is reactive and could easily ignite when heated in JSS than JFH. Other raw biomass with the high volatile matter according to Chen *et al.*, 2015 are bagasse (80.7 %), Leucaena (86.1 %), Microalgae (70.1 %), Oil palm fibre (72.5%), grass (82.4 %), rice husk (79.5%), sawdust (84.5%), spruce (85.2 %) which can be employed for thermochemical conversion.

Fixed Carbon

Fixed carbon is the solid combustible residue that remains after biomass is heated and the volatile matter is expelled. This is determined by subtracting the percentages of moisture, volatile matter and ash from the biomass sample. The fixed carbon calculated for JSS and JFH is 14.42 % and 18.63 % respectively. There are variations in values of fixed carbon reported in various studies for JSS and JFH. The fixed carbon reported by various studies from other countries are as follows: 24.99 % (Singh *et al.*, 2008) India, 11.27 % (Sricharoenchaikul and Atong, 2009) Thailand. The same observation was observed in the values of fixed carbon reported for JFH: 16.38 % (Singh *et al.*, 2008) India.

Higher Heating (Calorific) value (HHV)

The Higher heating values obtained are 17.37 and 13.80 MJ/Kg for JSS and JFH respectively. The Higher heating value is the amount of heat energy, which is emitted by biomass at the time of combustion under set conditions of the

experiment and it specifies the total energy potential obtainable in the biomass (Odetoye *et al.*, 2018). The HHV of Nigerian JSS is higher than 16.93 MJ/Kg (Singh *et al.*, 2008) and 16.50 MJ/Kg (Kratzeisen and Muller, 2009) and thus similar to wood which is the main source of energy in developing countries until now. The reported JFH HHV of 15.75 MJ/Kg by Singh *et al.*, 2008 as compared to 13.80 MJ/Kg in this study may be due to the method employed in drying the biomass sample. The longer the drying time, the lower the moisture content and the higher the calorific value. Therefore, any biomass that is intended for thermochemical conversion should be allowed to dry.

Effects of pretreatment on JSS and JFH biomasses

The effects of acid and alkaline pretreatments on JSS and JFH biomasses were studied to bring to light how chemicals changed the biomass structure. Both H₂SO₄ and NaOH could effectively degrade hemicellulose and break or weaken the linkages between lignin and hemicellulose. Furthermore, NaOH could effectively remove or lessen lignin (depending on the concentration used), whereas H₂SO₄ removes more hemicellulose (Isaac *et al.*, 2018).

During acid pretreatment, a significant reduction of the hemicellulosic component of JSS and JFH was hydrolysed, resulting in a mass loss of recovered biomass coupled with a consequential reduction of the cell wall thickness as compared to untreated biomasses. This observation corroborates Isaac *et al.*, 2018 in their recent work. From their research findings, they submitted that acid pretreatment caused degradation of polymer linkages and selective lignin removal, as well as relocation in specific ultrastructural layers of the secondary cell walls. The solid loss recorded in JSS and JFH could be due to the degradation of cellulose as the hemicellulose was removed, thereby making the cellulose component more accessible to acid.

Other researchers have reported similar findings (Xu *et al.*, 2011; Hosgun and Bozan, 2020).

A significant change in the crystalline structure was noticed in the alkali pretreated JSS and JFH as compared to untreated or raw samples. The improved crystallinity could be attributed to the aggregation of cellulose in NaOH solution (Xu *et al.*, 2012) because increased temperature (109 °C in this case) favoured cellulose aggregation. A significant increase in crystallinity of the dark-stained JSS was noticed. Alkali treatment of the JSS and JFH changes the cellulose structure via cellulose swelling that leads to a reduction in crystallinity and degree of polymerization of biomasses, by increasing their internal surface area (Iroba *et al.* 2013). The alkali treatment lessens lignin and hemicelluloses (the hemicelluloses polymers with more branches have stronger hydrophilic tendencies and are dissolved more easily in alkali media), thereby increasing the hydrophilicity of the JSS and JFH cellulose in alkali media, and this is ascribed to the abundance of its hydroxyl groups (-OH) because the induced chemical potential between the accessible hydroxyls of the hemicellulose, cellulose and polar water molecules leads to hydrogen bond formation. According to Gassan and Bledzki, 1998, the bound water results in the separation of cellulose fibrils and hydro expansion. Also, pores were observed in the JSS and JFH biomass matrix which is ascribed to the swelling instituted by NaOH, as these pores magnify the reactivity of the biomass matrix to any externally added material (Iroba *et al.* 2013). This swell is due to the disruption of intermolecular hydrogen bonds that binds cellulose molecules together (Oriez *et al.*, 2020). Biomass swell is more pronounced in JFH than JSS. The addition of NaOH to lignocellulosic biomass causes swelling within the structure, the mechanism is the interaction of alkali and lignocellulosic biomass causing saponification of intermolecular ester bond linkages within the biomass (Iroba *et al.* 2013). These observations agree with previous studies on

biomass structural deconstruction using the alkali pretreatment method (Iroba *et al.* 2013; Crawshaw *et al.*, 2002; Yang *et al.*, 2009). A solid loss was also observed in JSS and JFH biomasses after alkali pretreatment. This may be due to structural separation, disruption and disaggregation by the interaction between JSS and JFH biomass and NaOH solution at the elevated heating condition leading to the deconstruction or fractionation of the lignified matrix and hydrophilicity of cellulose. Two major reactions occurred during the alkali treatment of JSS and JFH biomasses. These two major reactions are solvation and saponification. During the pretreatment process, some portion of lignin is broken down, degraded and solubilized. Baruah *et al.*, 2018 concluded that a saponification reaction takes place throughout the alkali pretreatment process which causes cleavage of the intermolecular ester linkages between hemicellulose and lignin and results in solubilisation of lignin and hemicellulose fragments in the alkali solution. Similar solid loss via alkali pretreatment has been reported (Xu *et al.*, 2012; Iroba *et al.* 2013). Table 2 below summarises the yield and percentage loss of JSS and JFH biomasses during and after pretreatment.

Table 2: Biomass solid yield and percentage loss on pretreatment.

Biomass sample	Biomass weight		Solid yield (%)	Percentage loss on pretreatment
	Before pmt	After pmt		
Acid hydrolysed JSS	500	430	86.20	13.80
Alkali hydrolysed JSS	500	444	88.80	11.20
Acid hydrolysed JFH	500	325	65.00	35.00
Alkali hydrolysed JFH	500	265	53.00	47.00

*pmt -pretreatment

Where solid yield is calculated as

$$\text{Solid Yield} = \frac{\text{Weight of the biomass after pretreatment}}{\text{Original weight of biomass feed}} \times 100$$

Percentage loss is calculated as the difference between the weight of the biomass before and after pretreatment divided by the original weight of the biomass X 100.

Pyrolysis of *Jatropha curcas L.* biomasses

Table 3 show the results of slow pyrolysis of 1 Kg of JSS and JFH at 450 °C using a fixed bed reactor is presented below

Table 3: Mass of bio-oil (viscous and aqueous layers) and bio-char recovered from 1Kg *Jatropha* biomass feedstock

Pyrolysis products	Biomass sample (g)	
	JSS	JFH
Condensate (raw)		
Viscous phase	76.00	50.00
Aqueous phase	127.00	117.00
Biochar	152.00	250.00
Condensate (acid hydrolysed)		
Viscous phase	53.00	16.00
Aqueous phase	211.00	57.00
Biochar	398.00	150.00
Condensate (alkali hydrolysed)		
Viscous phase	70.00	27.00
Aqueous phase	169.00	51.00
Biochar	400.00	200.00

Yield of condensate (bio-oil viscous and aqueous layers) and bio-char

Pyrolysis products are condensate (which comprises of bio-oil viscous layer and aqueous phase), solid (in form of bio-char) and non-condensable gases. The product yields of pyrolysis of JSS and JFH at 450 °C, 1.14 mm particle size are presented in Table 3. Meanwhile, it is important to state that gas products resulting from the pyrolysis of JSS and JFH were not quantified in this work.

Table 4: Percentage by mass of bio-oil (viscous and aqueous layers) and bio-char recovered from *Jatropha* biomass feedstocks

Pyrolysis products	Biomass sample (%)	
	JSS	JFH
Condensate (raw)		
Viscous phase	7.60	5.00
Aqueous phase	5.30	1.60
Bio-char	5.30	2.70
Condensate (acid hydrolysed)		
Viscous phase	12.90	11.70
Aqueous phase	21.10	5.70
Biochar	16.90	5.10
Condensate (alkali hydrolysed)		
Viscous phase	15.20	25.00
Aqueous phase	39.80	15.00
Biochar	40.00	20.00

The yields of both untreated and pretreated JSS and JFH are relatively low. Untreated JSS pyrolysis yielded 15.20, 39.80, 40.00 % and 25.00, 15.00 and 20.00 % bio-char for raw, acid and alkali-treated JSS and JFH respectively. Raw (untreated) JSS gave a bio-oil yield of 7.60 %, which is higher than 5.00 % in the untreated JFH. The acid-treated and alkali-treated JSS gave the same bio-oil yield of 5.30 %, which is lower compare to 1.60 and 2.70 % in JFH. A critical look at Table 3 shows that the bio-oil aqueous layer yield is higher than the viscous layer: 12.90, 21.00 and 16.90 % for raw, acid-treated and alkali-treated JSS and 11.70, 5.70 and 5.10 % for raw, acid-treated and alkali-treated JFH respectively. This low yield reported in this study agrees with the report of Hsieh *et al.*, 2015 where untreated rice straw pyrolysis yielded 47 % bio-char, 26 % liquid with 4 % bio-oil and 17 % gas by mass and the acid-pretreated rice straw yielded 50 % bio-char, 28 % liquid with 2 % bio-oil and 15 % gas by mass. Generally, fast pyrolysis gives a greater bio-oil yield than slow pyrolysis.

Pretreatment with H₂SO₄ promoted increased bio-oil yield in JSS. The JSS bio-oil aqueous layer was 21.10 % as compared to 12.90 % and 16.90

% in raw and alkali hydrolysed JSS. For the JFH, 5.70 % bio-oil aqueous layer was higher than 5.10 % in alkali hydrolysed JFH.

Conversely, pretreatment with sodium hydroxide promoted bio-char formation in JSS. Biochar produced from the pyrolysis of JSS was 40 % as compared to 39.80 and 15.20 % in the acid-treated and raw JSS respectively. For the JFH, the raw sample gave the highest biochar (25 %), followed by the alkali hydrolysed JFH (20 %). Therefore, acid pretreated samples produced bio-oil with high value-added chemicals. This observation in bio-oil yield and bio-char formation, especially in JSS pyrolysis with acid and alkali pretreated biomass is in agreement with findings on a similar biomass feedstock used for pyrolysis (Mohammed *et al.*, 2016). Because a large percentage of lignin, which is an essential component of lignocellulosic biomass is removed during alkaline pretreatment, alkaline pretreatment cannot be considered suitable for a pyrolysis process. This observation corroborates Mohammed *et al.*, 2016 in their recent findings on the effect of deionized water, sulphuric acid, and sodium hydroxide pretreatments of Napier grass on pyrolysis oil characteristics.

GC-MS of Pyrolyzed *Jatropha curcas L.* biomass waste

The compositions of bio-oil produced from raw and pretreated JSS and JFH were analyzed by GC-MS as listed in Tables 5-10. Identification of the GC-MS peaks was based in most cases on comparison with spectra of the NIST 1998 spectrum library. Only those separated products and the most abundant compound found are listed. Generally, bio-oil is a complicated organic compound that consists of water, acids and heterocyclic substances (Ji-lu *et al.*, 2007), as these acids are the reason bio-oil pH is less than 3. The most abundant compound found in the viscous bio-oil are phenols: 52.63, 21.43 and 8.33 % in the untreated (raw), acid hydrolysed, alkali hydrolysed JSS and paraffin respectively: 25.00,

33.33 and 35.71 % in the untreated (raw), acid hydrolysed and alkali hydrolysed JFH respectively. The similarity in chemical composition was noticed in the raw, acid hydrolysed and alkali hydrolysed JSS with the presence of Phenol, 4-ethyl-2-methoxy-. Also, Hexadecanoic acid was present in the raw, acid hydrolysed and alkali hydrolysed JFH. The breakdown of the compounds detected in the Bio-oil produced from the six samples were classified into Paraffins, Olefins, Aromatics, Oxygen-containing compounds, Nitrogen-containing compounds, Phenols, Acids and Furan. The Oxygen-containing compounds (O.C.Cs) comprised of ester, alcohol, cyano and ketone while Nitrogen-containing compounds (N.C.Cs) consists of amide, nitrile, amine and nitroso- are as shown in Table 11 -12.

Gas Chromatography- Mass Spectrometry (GC-MS) of the Bio-Oil

The chromatograms of the raw JSS and JFH and the hydrolysed samples – acid and alkali are shown in Figs 1 – 6.

Table 5-10 is a list of compounds identified in the untreated (raw), acid hydrolysed and alkali hydrolysed Bio-oils from JSS and JFH respectively and Table 8-9 shows the breakdown of compounds detected in terms of percentage in the samples. The compounds detected in the Bio-oil produced from the six samples were classified into Paraffins, Olefins, Aromatics, Oxygen-containing compounds, Nitrogen-containing compounds, Phenols, Acids and Furan. The Oxygen-containing compounds comprise ester, alcohol, cyano and ketone while Nitrogen-containing compounds consist of amide, nitrile, amine and nitroso-. The untreated (raw) JSS Bio-oil sample produced a relatively high percentage of Phenols (52.63 %), while the acid hydrolysed and alkali hydrolysed samples produced only 21.43 % and 8.33 % respectively. The Bio-oil from the alkali hydrolysed JSS produced 50 % olefins, whereas olefins were absent in the raw

and acid hydrolysed samples. A higher percentage of aromatics (42.86 %) were identified in the acid hydrolysed Bio-oil sample, while only 10.52 % and nil were found in the untreated (raw) JSS and alkali hydrolysed JSS respectively. Furan (2 – Furancarboxaldehyde, 5-methyl-) was found only in the Bio-oil produced from the acid hydrolysed

JSS but absent in the untreated and alkali hydrolysed JSS.

Fourier Transform Infrared (FT-IR) Spectroscopy of the Bio-Oil / Analysis

The infrared spectra of the raw JSS, JFH and the hydrolysed samples – acid and alkali are shown in Figs 7-12.

Table 5: Chemical constituents of raw (untreated) Jatropha seed shell (JSS) detected by GC-MS

S/N	Retention time (min.)	Peak area (%)	Compound name
1.	4.497	3.04	Phenol
2.	5.881	1.04	Phenol, 2-methyl-
3.	6.328	3.06	Phenol, 4-methyl-
4.	6.690	22.08	Phenol, 2-methoxy-
5.	8.818	3.36	Phenol, 3-ethyl-
6.	9.517	6.20	Phenol, 2-methoxy-4-methyl-
7.	12.337	25.32	Phenol, 4-ethyl-2-methoxy-
8.	14.996	2.02	Phenol, 2,6-dimethoxy-
9.	15.500	2.62	Phenol, 2-methoxy-4-propyl-
10.	16.432	1.39	Butanamide
11.	17.014	0.87	6H-Pyrazolo[1,2-a][1,2,4,5] tetrazine hexahydro-2,3-dimethyl
12.	17.098	0.78	Benzyl alcohol, p-hydroxy—alpha.-(methylamino methyl)-
13.	18.547	0.81	3,3'-Bis(1,2,4-oxadiazolyl)-5,5'-diamine
14.	18.663	2.73	Phenol, 2-methoxy-4-(1-propenyl)
15.	20.190	1.29	Tetratetracontane
16.	21.173	12.96	Methyl 10-methyl-undecanoate
17.	21.510	4.88	5-tert-Butylpyrogallol
18.	32.493	1.71	Hexacosylheptafluorobutyrate
19.	36.911	3.81	Tetradecanoic acid

Table 6: Chemical constituents of acid hydrolysed JSS detected by GC-MS

S/N	Retention time (min.)	Peak area (%)	Compound name
1.	4.277	2.54	2-Furancarboxaldehyde, 5-methyl-
2.	4.471	5.28	Phenol
3.	5.286	0.54	Benzene,1-methyl-2-(1-methylethyl)-
4.	5.771	1.82	Benzene,1-ethynyl-4-methyl-
5.	5.868	5.18	Phenol, 3-methyl-
6.	6.321	17.49	Phenol, 4-methyl-
7.	8.275	8.88	Phenol, 2,4-dimethyl-
8.	9.368	6.08	Azulene
9.	10.235	0.87	1H-Benzimidazole, 2-ethyl-
10.	10.623	0.84	Folic acid
11.	12.343	4.65	Phenol, 4-ethyl-2-methoxy-
12.	12.958	11.06	Naphthalene, 1-methyl-
13.	13.547	3.55	Naphthalene, 1-methyl-
14.	15.759	0.59	(1-Methylpenta-1,3-dienyl) benzene
15.	16.154	1.38	1-Heptadecanamine
16.	16.406	0.58	Isobutyryl urea
17.	16.923	1.74	Naphthalene,1,3-dimethyl-
18.	17.434	0.78	Naphthalene,2,3-dimethyl-
19.	17.570	0.53	Naphthalene,2,3-dimethyl-
20.	18.637	6.33	Phenol, 2-methoxy-4-(1-propenyl)
21.	19.258	0.53	Ethanamine, 2-phenoxy-
22.	19.879	2.23	3-Azabicyclo[3.2.2]nonane, 3-nitroso-
23.	20.177	0.82	d1-Alanylglycylglycine
24.	21.173	9.63	Dodecanoic acid
25.	21.561	0.78	Naphthalene,1,6,7-trimethyl-
26.	23.644	1.15	Pyrimidine,4-fluoro-6-dimethylamino-
27.	28.489	3.55	Methyl tetradecanoate
28.	36.847	0.61	1-Heptadecanamine

Table 7: Chemical constituents of alkali hydrolysed JSS detected by GC-MS

S/N	Retention time (min.)	Peak area (%)	Compound name
1.	12.636	8.70	Phenol,4-ethyl-2-methoxy
2.	19.873	4.74	1-Pentadecene
3.	20.151	13.06	Pentadecene
4.	23.618	3.82	1-Tridecene
5.	23.871	3.45	Hexadecane
6.	26.697	7.64	8-Heptadecene
7.	26.924	5.97	1-Hexadecene
8.	27.247	3.07	1-Nonadecene
9.	27.493	9.19	Heptadecane
10.	31.025	1.08	1-Heptadecanamine
11.	35.572	9.69	Pentadecanenitrile
12.	36.860	29.59	Hexadecanoic acid

Table 8: Chemical constituents of raw (untreated) Jatropha fruit hull (JFH) detected by GC-MS

S/N	Retention time (min.)	Peak area (%)	Compound name
1.	20.184	14.45	Pentadecane
2.	21.167	38.02	Dodecanoic acid
3.	28.489	17.10	Methyl tetradecanoate
4.	35.372	2.19	2,4-Bis(hydroxyamino)-5-nitropyrimidine
5.	35.915	1.24	2,4-Dimethylamphetamine
6.	36.368	1.15	4-Thia-1-azabicyclo[3.2.0]heptanes-2-carboxylic acid, 6-amino-3,3-dimethyl-7-oxo-, [2s-(2.alpha.,5.alpha.,6.beta.)]
7.	36.905	24.62	Hexadecanoic acid
8.	38.102	1.24	2-Amino-1-(o-methoxyphenyl)propane

Table 9: Chemical constituents of acid hydrolysed JFH detected by GC-MS

S/N	Retention time (min.)	Peak area (min.)	Compound name
1.	4.491	2.77	Phenol
2.	5.584	5.11	2-Cyclopenten-1-one, 2,3-dimethyl
3.	5.875	5.28	Phenol, 2-methyl-
4.	6.347	4.49	Phenol, 4-methyl-
5.	8.281	25.01	Phenol, 2,4-dimethyl-
6.	11.781	2.69	2,4-Dimethylanisole
7.	12.344	5.84	Phenol, 4-ethyl-2-methoxyl-
8.	12.777	2.59	Tridecane
9.	16.134	1.86	5-Tetradecane, (E)-
10.	16.419	7.15	Tetradecane
11.	19.905	2.46	1-Pentadecene
12.	20.184	6.19	Pentadecane
13.	21.477	2.86	Benzene, 1,1 ¹ -ethylidenebis
14.	23.916	3.78	Hexadecane
15.	27.512	4.40	Heptadecane
16.	27.920	0.81	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
17.	28.625	5.40	4-Nonene, 5-butyl-
18.	31.057	2.75	Octadecane
19.	35.398	3.16	Tetradecane
20.	35.618	1.78	3-Ethyl-4-hydroxy-4,6,6-trimethylhexahydropyrimidin-2-thione
21.	36.892	3.63	Hexadecanoic acid

Table 10: Chemical constituents of alkali hydrolysed JFH detected by GC-MS

S/N	Retention time (min.)	Peak area (min.)	Compound name
1.	5.571	1.63	Isopropenylcyclopropane
2.	6.328	2.29	Phenol, 3-methyl-
3.	6.690	5.35	Mequinol
4.	8.255	12.78	Phenol, 3,5-dimethyl-
5.	12.318	7.43	o-Methoxy-.alpha.-methyl benzyl alcohol
6.	19.867	1.51	Cyclodecane
7.	20.145	3.34	Pentadecane
8.	21.451	1.91	Benzene,1,1'-ethylidenebis-
9.	27.241	1.69	3-Trifluoroacetoxytetradecane
10.	27.487	3.35	Heptadecane
11.	28.567	1.75	Ethyl dibromoacetate
12.	33.198	47.34	11-Octadecenoic acid
13.	36.310	3.82	Octadecenoic acid
14.	36.840	5.79	Hexadecanoic acid

Table 11: Breakdown of compounds detected in terms of percentage in the untreated (raw), acid hydrolysed and alkali hydrolysed JSS

S/N	Compounds detected	Percentage of Compounds detected (%)		
		Raw (untreated)	Acid hydrolysed	Alkali hydrolysed
1.	Paraffins	5.26	0.00	16.67
2.	Olefins	0.00	0.00	50
3.	Aromatics	10.52	43.86	0.00
4.	O.C.Cs	21.05	3.57	8.33
5.	N.C.Cs	5.26	17.86	8.33
6.	Phenols	52.63	21.43	8.33
7.	Acids	5.26	10.71	8.33
8.	Furan	0.00	3.57	0.00

Table 12: Breakdown of compounds detected in terms of percentage in the untreated (raw), acid hydrolysed and alkali hydrolysed JFH

S/N	Compounds detected	Percentage of Compounds detected (%)		
		Raw (untreated)	Acid hydrolysed	Alkali hydrolysed
1.	Paraffins	25.00	33.33	35.71
2.	Olefins	0.00	14.29	0.00
3.	Aromatics	25.00	14.29	7.14
4.	O.C.Cs	12.50	4.76	14.29
5.	N.C.Cs	12.50	0.00	0.00
6.	Phenols	0.00	28.57	14.29
7.	Acids	25.00	4.76	14.29
8.	Furan	0.00	0.00	0.00

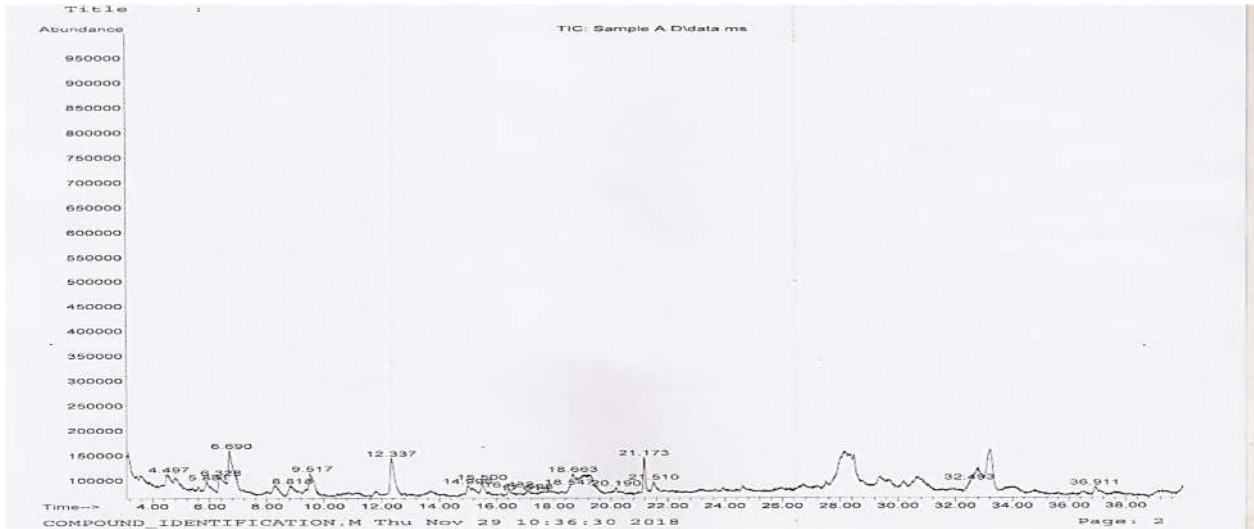


Fig 1: GC-MS chromatograms of the raw (untreated) JSS

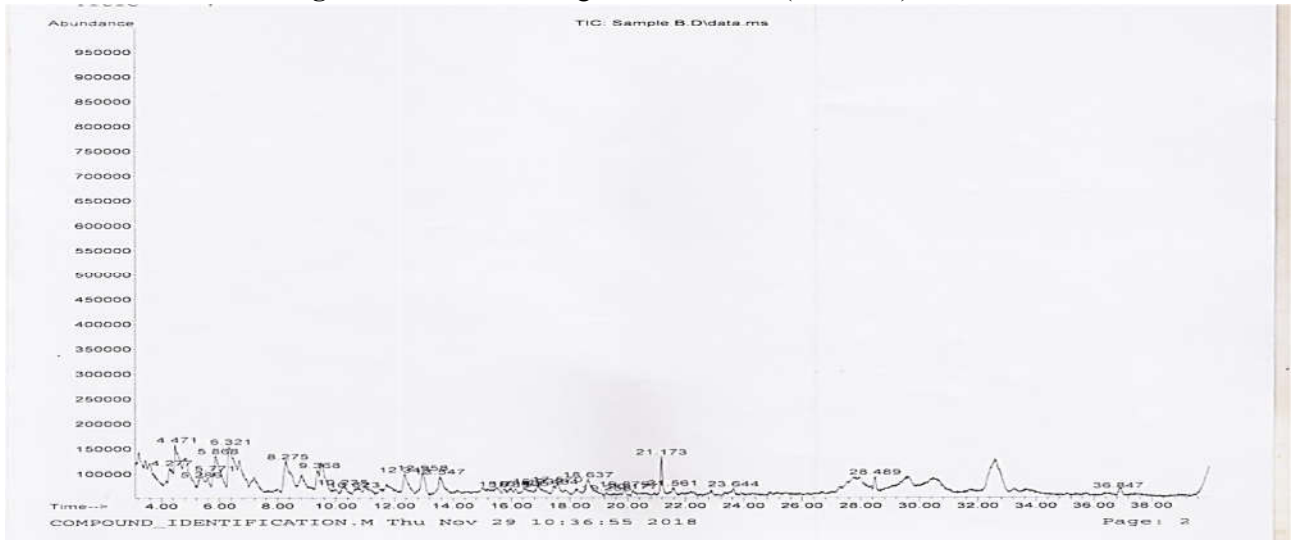


Fig 2: GC-MS chromatograms of the acid hydrolysed JSS

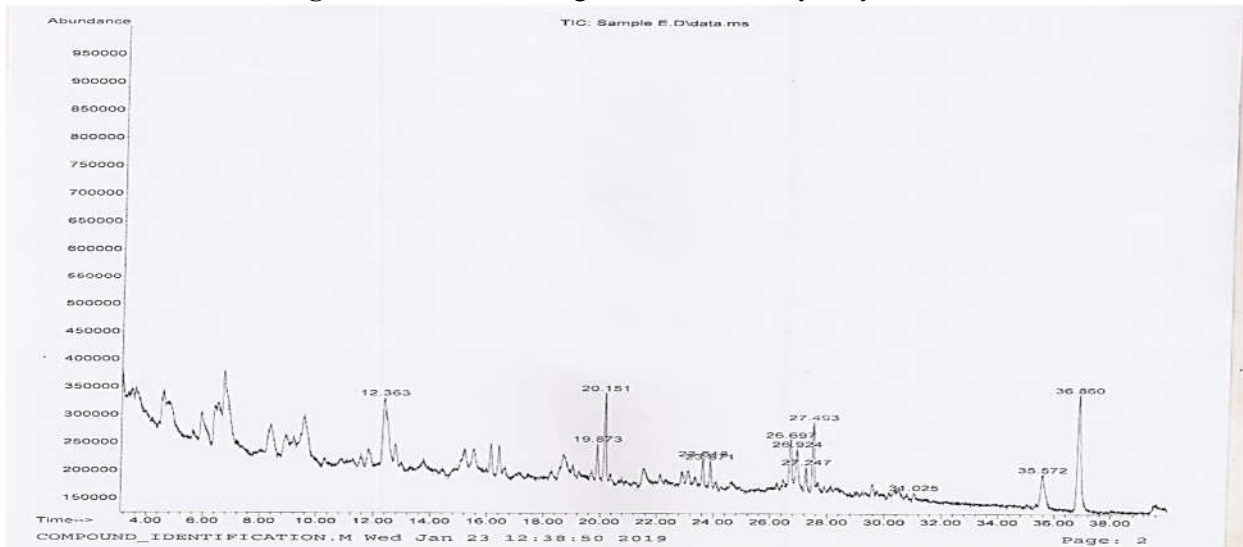


Fig 3: GC-MS chromatograms of the alkali hydrolysed JSS

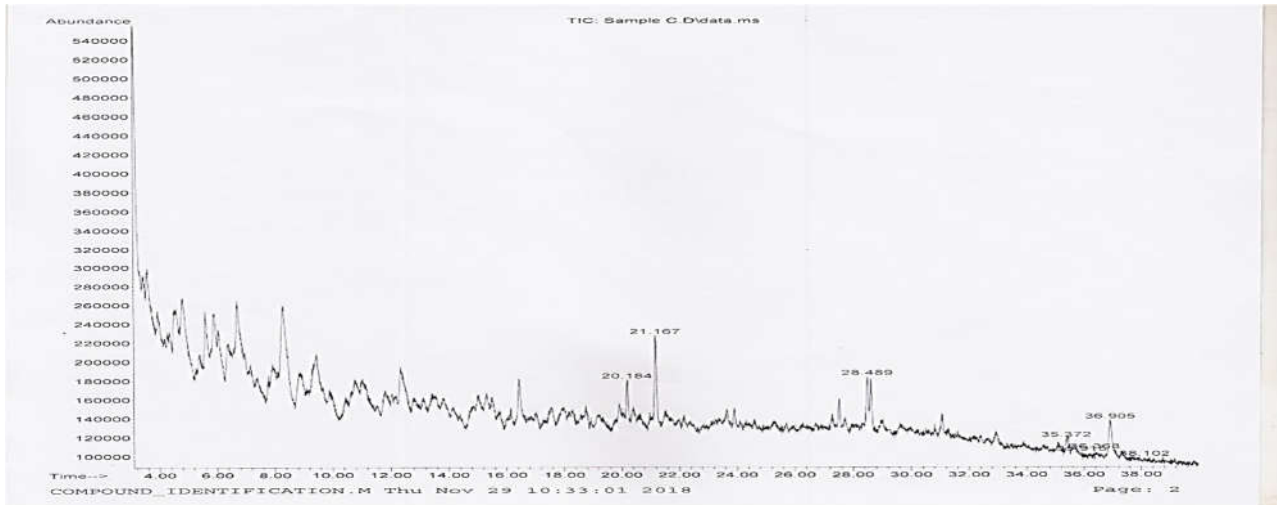


Fig 4: GC-MS chromatograms of the raw (untreated) JFH

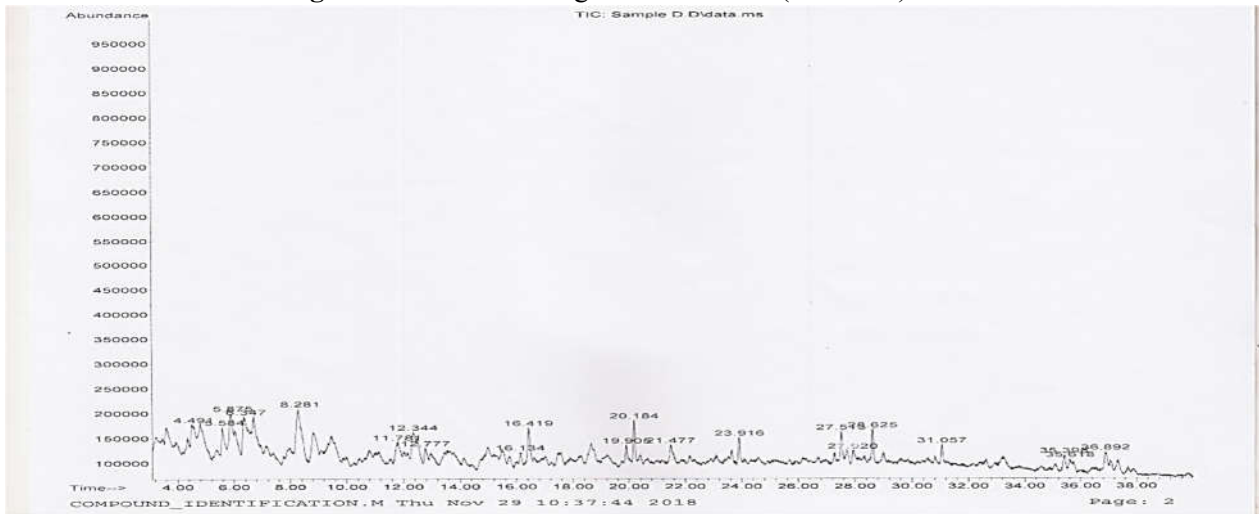


Fig 5: GC-MS chromatograms of the acid hydrolysed JFH

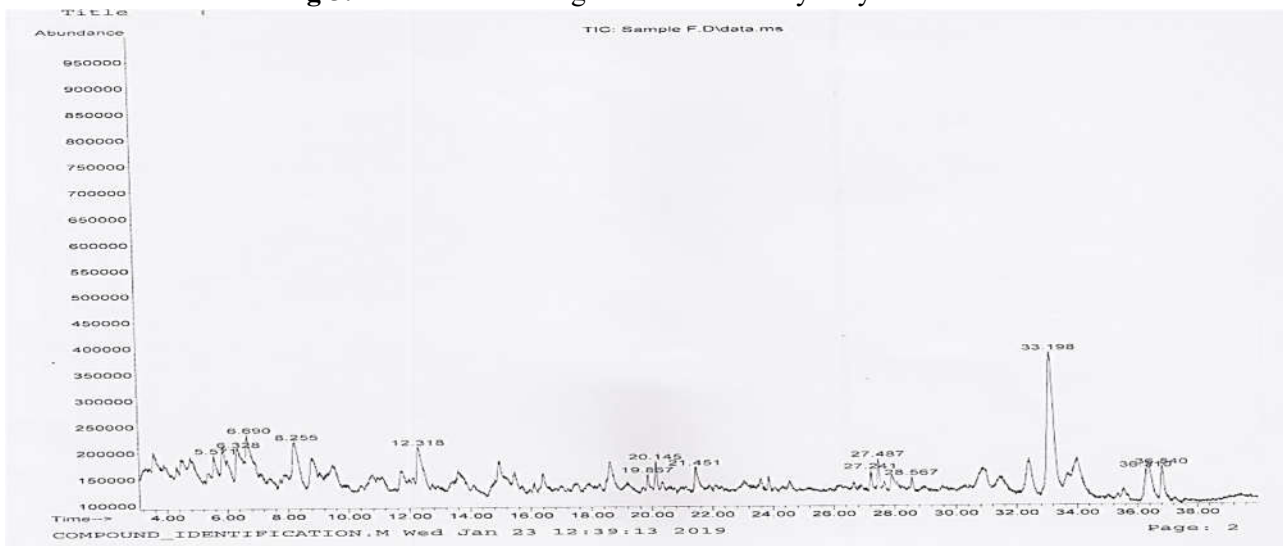


Fig 6: GC-MS chromatograms of the alkali hydrolysed JFH

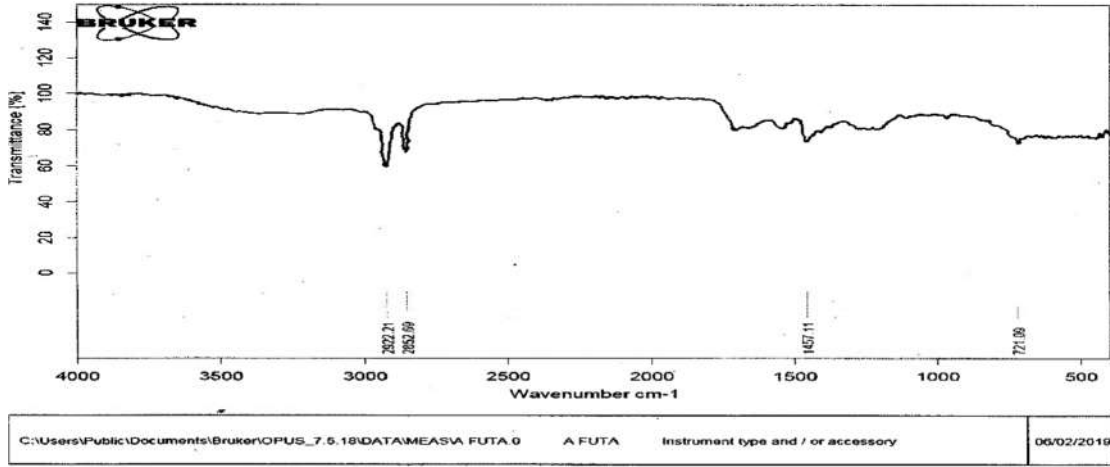


Fig. 7: FT-IR Spectrum for raw (untreated) JSS Bio-oil

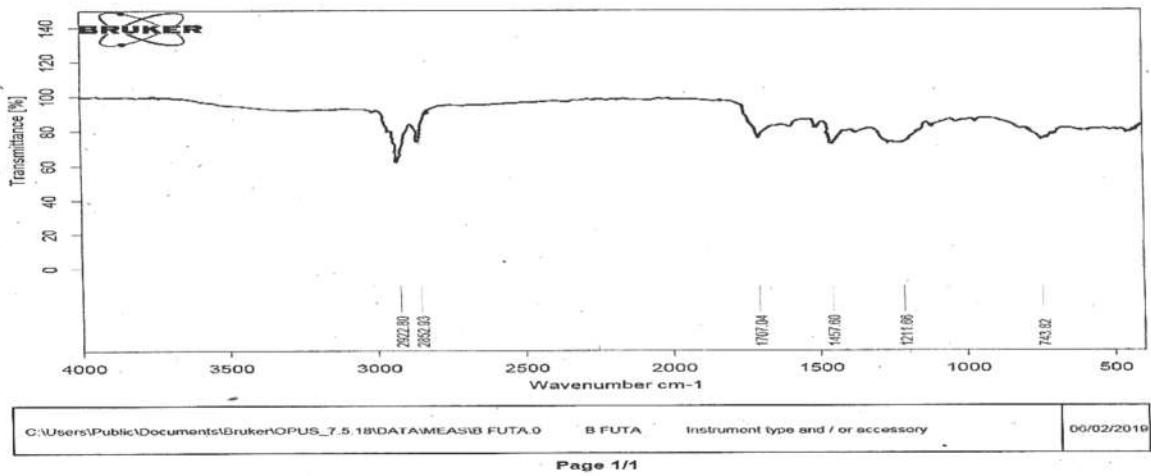


Fig. 8: FT-IR spectrum for acid hydrolysed JSS Bio-oil

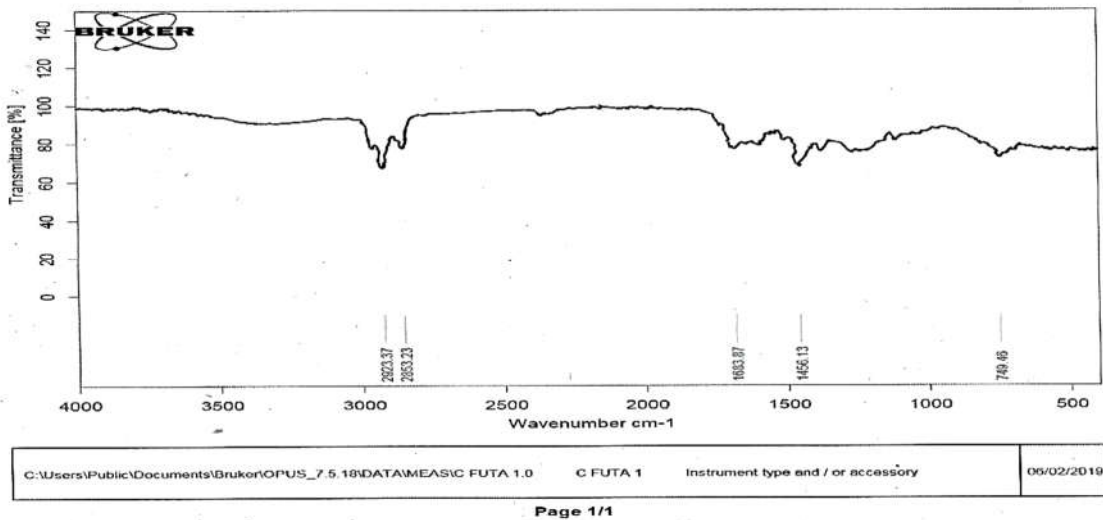


Fig. 9: FT-IR spectrum for alkali hydrolysed JSS Bio-oil

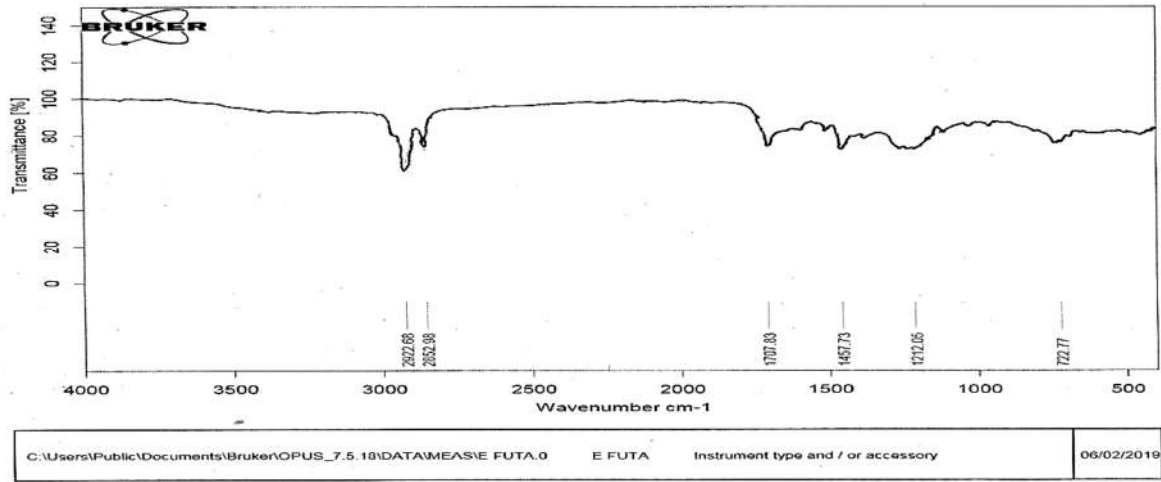


Fig. 10: FT-IR spectrum for raw (untreated) JFH Bio-oil

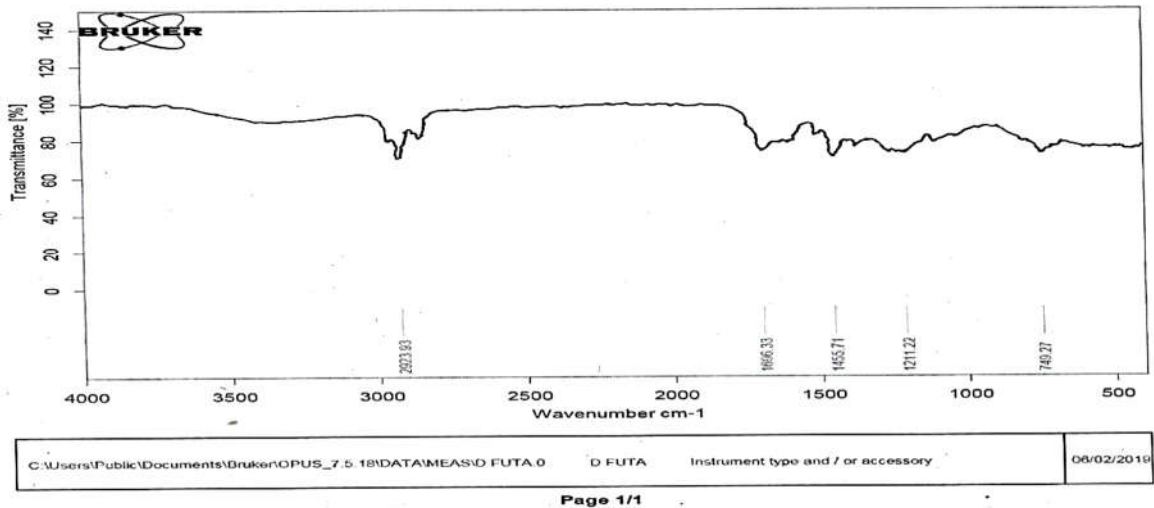


Fig.11: FT-IR spectrum acid hydrolysed JFH Bio-oil

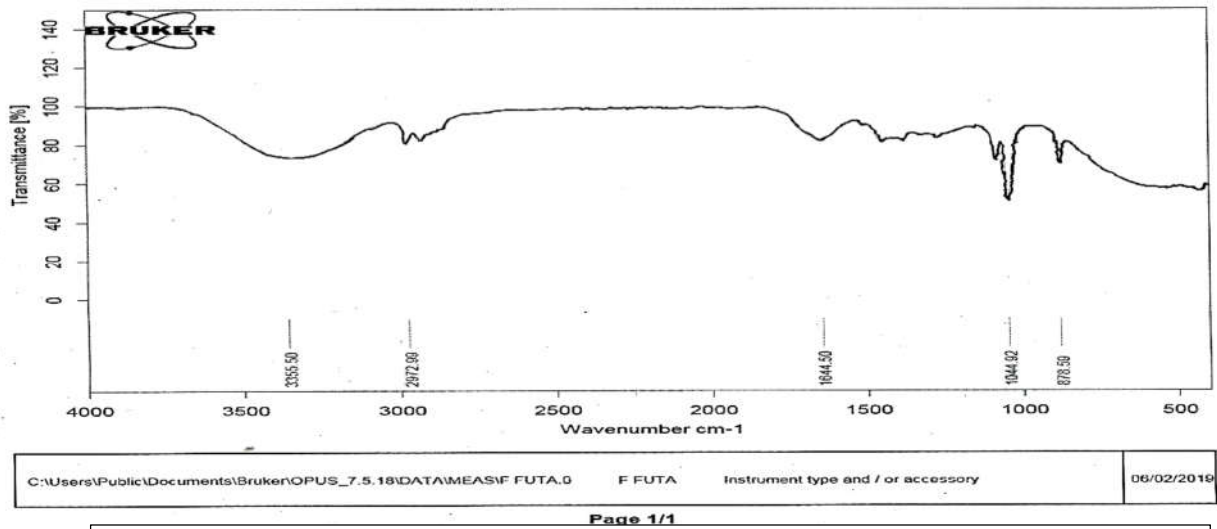


Fig.12: FT-IR spectrum alkali hydrolysed JFH Bio-oil

Table 10: Characteristics IR absorption frequencies of Organic functional groups of raw, acid and alkali hydrolysed *Jatropha curcas* L. seed shell (JSS)

	Characteristics absorption (cm^{-1})			Functional group/Type of vibration
	Raw	Acid hydrolysed	Alkali hydrolysed	
1.	2922.21	2922.80	2922.68	C-H (alkane) /stretching
2.	2852.69	2852.93	2852.98	C-H (methylene)/asymmetrical stretching
3.	-	1707.04	1707.83	C=O (ketone, aliphatic and open chain R_2CO)/ stretching
4.	1457.11	1457.60	1457.73	C=C (aromatic) /stretching
5.	-	1211.66	1212.05	C-O (ethers,esters)/ stretching
6.	721.09	743.82	722.77	C-H (<i>cis</i> distributed olefins =C-H and $-(\text{CH}_2)_n$ methylene groups (<i>cis</i> distributed alkenes and olefins / out-of-plane bending overlapping rocking and out-of-plane bending vibration of methylene and alkene

Table 11: Characteristics IR absorption frequencies of Organic functional groups of raw, acid and alkali hydrolysed *Jatropha curcas* L. fruit hull (JFH)

Raw	Characteristics absorption (cm^{-1})		Functional group/Type of vibration
	Acid hydrolysed	Alkali hydrolysed	
1.	-	-	3355.50 O-H / stretching (H-bonded)
2.	2923.37	2923.93	2972.99 C-H (alkane)/stretching
3.	2853.23	-	- C-H (methylene)/ asymmetrical stretching
4.	1683.87	1693.33	- C=O (ketone, conjugated)
	-	-	1644.50 C=C (alkene)/ stretching
5.	1456.13	1455.71	- C=C (aromatic)/ stretching
	-	1211.22	- C-O (ether, esters)/ stretching
	-	-	1044.92 C-O-C (ether)/antisymmetric stretching
	-	-	878.59 C-H (arene)/ out-of-plane bending vibration
6.	749.46	749.27	- C-H (<i>cis</i> distributed olefins =C-H and $-(\text{CH}_2)_n$ methylene groups (<i>cis</i> distributed alkenes and olefins

The Bio-oil obtained from the raw and treated *J. curcas* L. biomass was characterized by infrared spectroscopy (FT-IR). The infrared spectra of the raw, acid hydrolysed and alkali hydrolysed JSS and JFH are shown in Figs 7-12. The reflectance bands were used to identify the main functional groups present. The band assignments of the spectra areas contained in Biomass pyrolysis previous studies (Wong *et al.*, 1998; Capunitan and Capareda, 2013; Mohammed *et al.*, 2014;

Sutrisno and Hidayat, 2016; Shah *et al.*, 2016a; Shah *et al.*, 2016b; Dhanavath *et al.*, 2017;). The summary of the characteristics IR absorption frequencies as well as the type of vibration of Organic functional groups of raw, acid and hydrolysed JSS and JFH biomasses are itemized in Tables 10 and 11.

The results of the raw, acid hydrolysed and alkali hydrolysed JSS at 2922.21, 2922.80 and 2922.68 cm^{-1} respectively indicates (C-H) alkane

stretching vibration while strong sharp peaks at 2852.69, 2852.93 and 2852.98 cm^{-1} respectively also indicate (C-H) methylene asymmetrical stretching. Distinctive strong peaks at 1707.04 and 1707.03 cm^{-1} for acid and alkali hydrolysed JSS respectively correspond to (C=O) ketone, aliphatic and open-chain stretching. Meanwhile, this distinctive peak was not observed in the raw JSS. The strong intensity due to stretching vibration of C=C (aromatic) appear at 1457.11, 1457.60 and 1457.73 cm^{-1} for raw, acid hydrolysed and alkali hydrolysed samples respectively. Absorptions possibly due to C-O vibrations from carbonyl components (ether, ester) occur at 1211.66 and 1212.05 cm^{-1} for acid and alkali hydrolysed samples respectively and this was observed to be absent in the raw JSS sample. The bands at 721.09, 743.82 and 722.77 cm^{-1} for raw, acid and alkali hydrolysed JSS samples respectively are related to an out-of-plane bending vibration of methylene and alkene assigned to C-H (*cis* distributed olefins, =C-H and $-(\text{CH}_2)_n$ methylene groups (*cis* distributed alkenes and olefins). The raw, acid and alkali hydrolysed JSS showed similar functional groups (C-H (alkane), C-H (methylene), C=C (aromatic) and C-H (*cis* distributed olefins =C-H and $-(\text{CH}_2)_n$ methylene groups (*cis* distributed) alkenes and olefins. However, C=O (ketone, aliphatic and open-chain R_2CO and C-O (ether, esters) were observed in the pretreated JSS. These functional groups were not observed in the raw (unpretreated) JSS. The FT-IR results showed that the raw JSS is deficient in oxygenated species. It can be concluded that both acid and alkali pretreatment enhances the emergence of more functional groups in the Bio-oil produced from the JSS. The appearance or disappearance of the functional group was due to the conversion of one class of compound into another class of compound due to dehydrogenation, dehydration and cracking during pyrolysis (Shah *et al.*, 2016).

The bands at 2923.37, 2923.93 and 2972.99 cm^{-1} for raw, acid hydrolysed and alkali hydrolysed JFH are related to C-H stretching vibrations, signalling the presence of alkanes. A peak at 2853.23 cm^{-1} for the raw JFH corresponds to C-H (methylene) asymmetrical stretching vibration. The band at 1683.87 cm^{-1} and 1696.33 cm^{-1} for raw and acid hydrolysed JFH corresponds to C=O stretching while a band at 1644.50 cm^{-1} for alkali hydrolysed sample can be assigned to C=C (alkene) stretching. A band at 1456.13 cm^{-1} and 1455.71 cm^{-1} for raw and acid hydrolysed JFH is assigned to C=C (aromatic) stretching. A distinctive band at 1211-22 cm^{-1} for acid hydrolysed JFH corresponds to C-O (ethers, esters) stretching vibration and another at 1044.92 cm^{-1} for alkali hydrolysed JFH corresponds to C-O-C (ether) antisymmetric stretching. A differential strong band peak at 3355.50 cm^{-1} for alkali hydrolysed JFH is assigned to O-H (H-bonding) stretching. A strong sharp peak at 878.59 cm^{-1} for the alkali hydrolysed JFH corresponds to C-H (arene) out-of-plane bending vibration. Medium peaks at 749.46 cm^{-1} and 749.27 cm^{-1} for raw and acid hydrolysed JFH respectively are assigned to C-H (*cis* distributed olefins, =C-H and $-(\text{CH}_2)_n$ methylene group out-of-plane bending overlapping rocking and out-of-plane bending vibration of methylene and alkene. Also, the result of the alkali hydrolysed JFH indicates (O-H) alcohol stretching at 3355.50 cm^{-1} . This O-H, which is a differential broad peak may be due to the presence of water content in the Bio-oil produced through the alkali hydrolysis process. The differential peak was not observed in the raw and the acid hydrolysed JFH Bio-oil.

Scanning Electron Microscopy (SEM) of the raw and hydrolysed samples used for Bio-oil Production

As biomass is being pretreated, all the surface characteristics of the hydrolysate change progressively. Scanning electron microscope

(SEM) micrographs of pretreated and untreated *Jatropha curcas* L. waste (JSS and JFH) were taken to study the changes in surface characteristics of the biomass. The images obtained at magnifications X1000 and X2000 are shown in Figs 13-14.

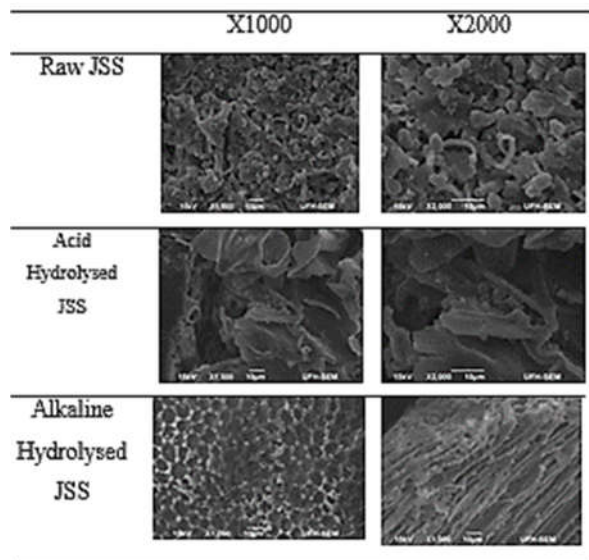


Fig. 13: SEM images of the raw (untreated), acid hydrolysed and alkali hydrolysed JSS at X1000 and X2000 magnifications

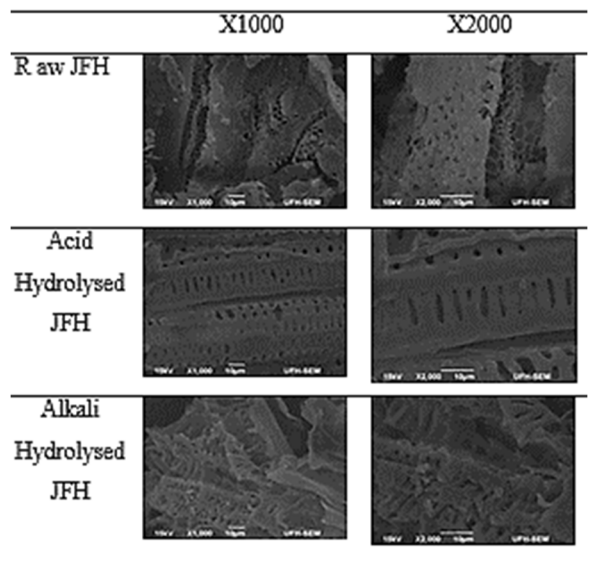


Fig.14: SEM images of the raw (untreated) JFH, acid hydrolysed and alkali hydrolysed JFH at X1000 and X2000 magnifications

For the JSS, the SEM images clearly showed that the raw (untreated) revealed a rigid and highly compact structure whereas in acid and alkali pretreated JSS, there is a reasonable surface modification and the biomasses showed the opening of the cellulose fibrils, thereby increasing the porosity of the biomass. Meanwhile, pores present in the acid and alkali-treated JSS may have been due to substantial removal of the hemicelluloses and lignin respectively. The possible reason for surface modification may be fractionation/breaking of lignin bond caused by NaOH activity in alkali pretreated JSS and JFH. According to Tsegaye *et al.*, 2016, the lignin-hemicellulose-cellulose matrix is cloven and destroyed by excited carboxyl groups produced by saponification of ester linkage on the xylan backbone which gives rise to hydrogen bonds disruption in the cellulose. The raw JSS image illustrates a large and highly dense structure which are coarsely grained with a larger contact area and increased roughness. It also disclosed that the particles are multidispersed with significant pore aperture. Nevertheless, the acid and alkali hydrolysed JSS showed short fibrous and porous structures from the initial connected structure and are fully exposed, thus broadening the external surface area and porosity. In alkali hydrolysed JSS image, the pores present may be due to high levels of removed lignin, which is in tandem with the observation of Wi *et al.*, 2015 in their similar work using alkali pretreatment.

Differences in morphology could be observed in the raw (untreated) and treated (hydrolysed) JFH biomass that had cracked, fibrous tissue with a relatively smooth surface. Fig. 14 shows that the acid hydrolysed JFH had some parallel cracks with an array of networks of particles that are highly packed. As could be seen on the acid hydrolysed JFH sample surface, the flocculent matter contains narrow pores spread across the structure and the pores are more obvious. The acid pretreatment effectively and efficiently

removed or lessened hemicellulose, which might have altered the interaction between cellulose and lignin, as this may be responsible for the pores present. The alkali hydrolysed JFH showed that the cracked fibre tissue on the surface of the raw and acid hydrolysed samples were ablated. The original surface was enhanced and the specific surface area was increased. The alkaline hydrolysed JFH contain a macroporous structure and new pores did not exist on its surface.

Conclusion

In this present study, *Jatropha curcas* L. fruit hull and seed shell, as well as their acid and alkali-pretreated biomasses were used as a novel raw material for the production of bio-oil via pyrolysis at 450 °C in a fix bed reactor. Both H₂SO₄ and NaOH could effectively degrade hemicellulose and break or weaken the linkages between lignin and hemicellulose. Furthermore, NaOH could effectively remove or lessen the lignin, whereas H₂SO₄ removed or lessened more hemicellulose. The removal or reduction of any lignin or hemicellulose is dependent on the concentration of acid or alkali used. GC-MS analyses of the raw and pretreated JSS and JFH revealed the presence of phenols, hydrocarbons and other essential chemical compounds like Furan (2 – Furancarboxaldehyde, 5-methyl-). The FT-IR results showed primary absorption bands that give fundamental knowledge of the type of chemical group present in the bio-oil of the raw and the pretreated pyrolysed JSS and JFH. The SEM photographs revealed the impact of pyrolysis on the raw and pretreated feedstocks. Meanwhile, the raw SEM micrograph showed a dense biomass structure, the pretreated biomass surface was damaged which therefore improved biomass porosity. Bio-oil thus obtained can be used as synthetic fuel after pretreatment (upgrading) or chemical feedstock after separation.

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Competing Interest

The authors declare no competing interests

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