Full Length Article

An upgraded bio-oil produced from sugarcane bagasse via the use of HZSM-5 zeolite catalyst

S.D. Rabiu [a], M. Auta [b],*, A.S. Kovo [b]

[a] Department of Chemical Engineering, Federal Polytechnic, Bida, Nigeria
[b] Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria

ABSTRACT

The pyrolysis upgrading of bio-oil from sugarcane bagasse (SB) using ZSM-5 zeolite catalyst was carried out in a fixed bed reactor to determine the effects of heating rate, temperature, and catalyst/biomass ratio on yield of bio-oil and their chemical compositions. Proximate analysis indicated that SB has 13.2% moisture content. The ultimate analysis carried out established that the percentage of carbon content is higher (48.2%) than oxygen content (44%) while the fibre content analysis showed 26.4% lignin, 33.3% cellulose, 30.1% hemicellulose. The heating rate, temperature and catalyst/biomass ratio were varied in the range of 10–50 °C/min, 400–600 °C and 0.05–0.25 respectively. The non-catalytic pyrolysis gave the maximum percentage yield (45.67 wt%) of bio-oil at a pyrolysis temperature of 600 °C, heating rate of 50 °C/min, sweeping gas flow rate of 40 mL/min and the catalytic pyrolysis gave 40.83 wt% of bio-oil at the same conditions. The FT-IR spectra showed that the non-catalytic bio-oil is dominated by oxygenated compounds (acids, ketones, aldehydes, alcohols), while the catalytic bio-oil had preponderances of desirable compounds (alkanes, alkenes, aromatics, phenols). The chemical composition of the bio-oils was analyzed using GC–MS, which revealed that the quality of the bio-oil has been improved using HZSM-5 catalyzed pyrolysis.

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1. Introduction

The majority of world's source of liquid fuel is still supplied by fossil fuel (non-renewable), their use has led to serious environmental problem such as global warming, atmospheric pollution and acid rain. The development of renewable energy such as solar, water and wind as well as biomass as replacement for fossil-based fuel is rapidly progressing. Biomass is organic materials derived plants (aquatic and terrestrial), woods, animal manures and vegetables that mainly consist of carbon, hydrogen, nitrogen and small portion of inorganic species [1]. It is an embodiment of energy synthesized with the aid of solar energy through photosynthesis process [2]. Biomass is a potential feed stock for fuel and chemicals production due to its availability, renewability and environmental friendliness [3]. It is an alternate source for carbon base liquid fuel than can help alleviate dependence on fossil fuels and mitigate global warming and other environmental issues associated with the

use of fossil fuels [4]. Biomass can be converted to bio-fuel via different thermal, biological and physical processes.

Among the biomass to energy conversion processes, pyrolysis is one of the most applied methods for obtaining valuable chemical fuels [5]. In addition, solid biomass and waste are very difficult and costly to manage which also gives impetus to pyrolysis (thermochemical heating of an organic material in the absence of air) research. The absence of oxygen in the process does not promote combustion of the biomass but the chemical compounds (cellulose, hemicellulose and lignin) that make up that material thermally decompose into combustible gases and chars through series of reactions which include cracking, cyclization or aromatization, and dehydrogenation. Thus pyrolysis of biomass produces three products which are liquids (tars or bio-oil), solid (bio-char) and low molecular weight gases (volatiles). The proportion of these products depends on several factors including the composition of the feed stock and process parameters. Bio-oils in general are dark brown organic liquids that are highly oxygenated, relatively unstable and chemically complex [6]. This bio-oil can be produced by non-catalytic pyrolysis or catalytic pyrolysis (upgrading). The non-catalytic pyrolysis produces low quality bio-oil that cannot be used in convectional diesel engine [7]. Because it contains

highly oxygenated compounds which result in high acidity, high viscous and high water content which make it unstable. Therefore the bio-oil produced by non-catalytic pyrolysis needs to be upgraded by the use of catalyst which will enhance the cracking reactions leading to the production of less viscous, higher heating value and better stable bio-oil [8].

Various catalysts have been used for catalytic pyrolysis activities. Dolomite as a catalyst is attracting global attention due to its abundance and inexpensive nature. Calcined dolomite was extensively investigated in fixed-bed solid waste and it greatly influenced the product yields by significantly increasing the amount of low molecular weight gases production while decreasing oil and char yield [9].

Alkali metals (Na_2CO_3 and K_2CO_3) catalysts were used in catalytic pyrolysis of rice husk for bio-oil production [10], and catalytic pyrolysis of palm kernal shell waste in fluidized bed using Ni-based catalyst Ni/SiO_2-N [11]. These Ni and alkali metal based catalysts were proven to be effective in heavy tar elimination and achieved more than 99% tar destruction, but were found to become inactive by carbon deposition [12].

More recently, the unique pore structure and activity of ZSM-5 distinctly makes it one of the leading catalysts available for aromatics and olefins production [13]. The ZSM-5 catalyst has a 3-dimensional pore structure with pore size of $8.9 \pm Å$ [14]. The ZSM-5 catalyst has internal acid sites in its pores which promote production of olefins and aromatics whereas; its external acid sites advances coke formation. This is due to larger molecular diameter of coke than ZSM-5 pores [13]. Modification of ZSM-5 catalyst aimed at pore widening, retention of internal acid sites, and increasing the selectivity of the catalyst surface is necessary so as to impede coke formation activities and facilitate desired products formation [15,16].

Sugarcane bagasse is a biomass crushed remnants of sugarcane after syrup extraction [17]. Sugarcane utilizes solar energy by means of photosynthesis, to grow and therefore produce biomass. During photosynthesis CO_2 is extracted from the air and this CO_2 is released back into the atmosphere during combustion rendering the whole process CO_2 neutral. This energy is then released either by means of natural decay, or it can be harvested by means of controlled combustion or chemical reactions. Bagasse is a lignocellulosic compound which implies that it contains varying amounts of cellulose, hemicellulose and lignin [18].

This study was aimed at production of upgraded sugarcane bagasse bio-oil by catalytic pyrolysis using zeolite socony (Standard Oil Company of New York) mobil-5 (ZSM-5). The effect of the pyrolysis fixed-bed operating conditions such as heating rate, pyrolysis temperature and catalyst/biomass ratio on the bio-oil was investigated. The sugarcane bagasse bio-oil was characterized with the aid of Fourier transform infrared and Gas chromatograph mass spectrometry analyses to determine the bioactive composition and quality of the product.

2. Materials and methods

2.1. Materials

The sugarcane bagasse was obtained from locally produced brown sweet (Alewa) factory in Bida, Local Government Area of Niger State, Nigeria. The bagasse was sun dried until a constant weigh was achieved, cut and ground to a particle size of 2 mm. The catalyst used was ZSM-5 zeolite, with a SiO_2/Al_2O_3 ratio of 80 and a surface area of 425 m^2/g supplied by Zeolyst International (Conshohocken, PA, USA). The catalyst was activated using ammonium hydroxide (NH_4OH) solution, oven dried at 105 °C overnight and then calcined at 550 °C for 6 h.

2.2. Feedstock characterization

The proximate analysis to determine the moisture content, ash content, fixed carbon and volatile matter, was carried out in National Cereal Research Institute (NCRI) Badeggi, Niger State, Nigeria. This was done in accordance with ASTM D3175 standard procedure. The ultimate analysis describing the elemental composition of Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur was carried out in accordance with the standard methods of the Association of Official Analytical Chemists (AOAC, 2003). The fibre content analysis to determine the lignin, cellulose, hemicellulose was done in accordance with ASTM D3175.

2.3. Methodology

The schematic diagram of a batch type vacuum pump reactor also known as carbon vapour depositor (CVD) used to carry out the non-catalytic and catalytic slow pyrolysis experiment is presented in Fig. 1. The experimental setup consists of a cylindrical reactor made up of horizontal glass (borax) tube furnace with length-1010 mm, internal diameter-60 mm and outer diameter-65 mm. The pyrolyzer was installed inside an electrical heater and was insulated to enable the heating of the reactor up to 1200 °C. The reactor is equipped with a sample holder (cubit) and connected to both vacuum and nitrogen source. The pyrolyzer effluent channel was connected to ice-trap immersed in ice-water bath to condense the pyrolysis vapours at 0–5 °C. The non-condensable gases were adsorbed in a bath of water.

Slow pyrolysis was adopted in all the experiments, 20 g of sugarcane bagasse (SB) were loaded into the cubit and fixed into the reactor. A vacuum pump was set to obtained high vacuum inside the pyrolyzer between 0.003 and 0.001 mmHg pressures (<atmospheric
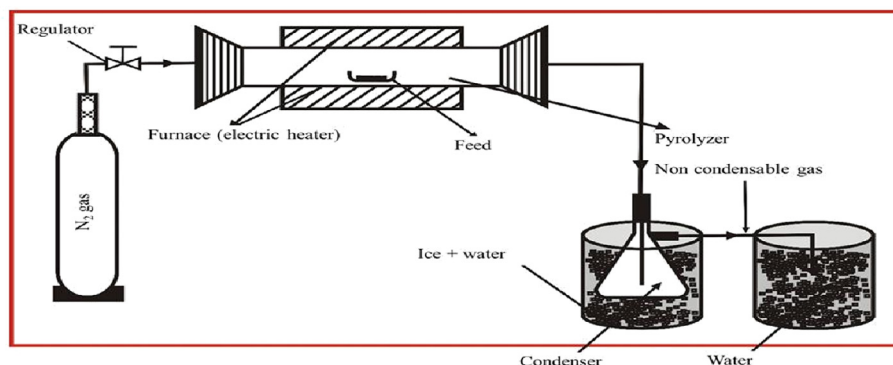

Fig. 1. The fixed-bed pyrolysis experimental setup.

pressure), the inertness of the reactor chamber was maintained by a constant flow of nitrogen gas at 40 mL/min. The experiments were performed in two ways, the non-catalytic and catalytic. In both cases, the pyrolysis process resulted in char, bio-oil and gas products. The fluid gas comes out through the vacuum line of the pyrolyzer and the solid char remain in the cubit as residue. The fluid from the pyrolyzer was then cool through the condenser. The condensate (bio-oil) was collected and stored in a sample bottle for further analysis, while the incondensable gases were absorbed in a water bath. Mass balance calculations were used to estimate yield; char (wt%) + bio-oil (wt%) + gas (wt%) = 100. Yields of char and bio-oil were determined based on change in weight of the cubit and the condenser respectively, before and after each experiment.

2.4. Effect of operating parameters on the bio-oil yield

Three operating parameters namely heating rate, pyrolysis temperature and catalyst/biomass ratio were investigated. The heating rate was varied at 10, 20, 30, 40 and 50 °C/min, for a constant temperature of 400, 500 and 600 °C, respectively; for 10 min in order to obtain the best heating rate. The catalyst/biomass ratio was varied at 0.05, 0.10, 0.15, 0.20 and 0.25 at constant heating rate and temperature of 50 °C/min and 600 °C respectively for 10 min.

2.5. Analysis of bagasse pyrolysis product (bio-oil)

Gas chromatograph mass spectrometry (GC–MS) analysis of the bio-oil was conducted using a Hewlett Packard HP 5890 series II Gas Chromatograph with an Agilent auto sampler and coupled to an HP 5972 detector. Helium was used as carrier gas with a DB 1706 non-polar capillary column. The initial oven temperature was 40 °C and rising up to 290 °C at a rate of 3 °C/min. The injection temperature was held at 310 °C with a volume of 5 mL. Identification of the GC–MS peaks was based on the NIST mass spectra library. The dilution solvent used was ethanol and the dilution ratio was 1:5.

Fourier transform infrared spectroscopy (FTIR) analysis was carried out using Perkin Elmer Frontier FTIR Spectrometer. In a typical analysis 0.07 g wafer of the sample consisting of 1% of the sample and 99% KBr window was used. The mixture was pressed under pressure of about 12 MPa to produce a thin film wafer. The wafer was inserted in the sample holder of the FTIR equipment, then, FTIR spectra of the sample was recorded from 4500 to 500 cm^{-1} with a 2 cm^{-1} resolution operated at scan speed of 0.125 cm^{-1} s^{-1}. Prior to the sample analysis background spectrum of air at ambient condition was ran.

3. Results and discussion

3.1. Characteristic features of sugarcane bagasse

The characteristic features of the sugarcane bagasse (SB) determined through proximate, ultimate and fibre content analyses are presented in Table 1. The ash content of the SB was moderately low indicating the viability of the biomass as a good potential precursor for fuel production. High ash content in biomass used for bio-oil production affect its burning rate, increase cost of processing, poor combustion and energy conversion, and also possess disposal problems [5]. Compounds of sulphur (SOx) and nitrogen (NOx) emanating from high elemental sulphur and nitrogen content in biomass, respectively; are known to cause toxic emissions to the environment during combustion [19]. The ultimate analysis (Table 1) revealed that the sugarcane bagasse has relatively insignificant composition of nitrogen (1.6 wt%) and sulphur (0.8 wt%). The high content of lignocellulose of the SB showed that the precursor has potential as carbon neutral source that can serve as substitute for petroleum base energy through its conversion to chemicals and liquid fuels [19].

3.2. Effect of heating rate on product yield for non-catalytic pyrolysis

The impact of various heating rates at constant temperature of 400, 500 and 600 °C was studied. The expected pyrolysis product yield in mass percentage were char, bio-oil and the gas are shown in Fig. 2. For a constant temperature of 400 °C and at varied heating rate of 10, 20, 30, 40 and 50 °C/min, the char decreased from 59.05

Table 1
Characterization of sugarcane bagasse (SB).

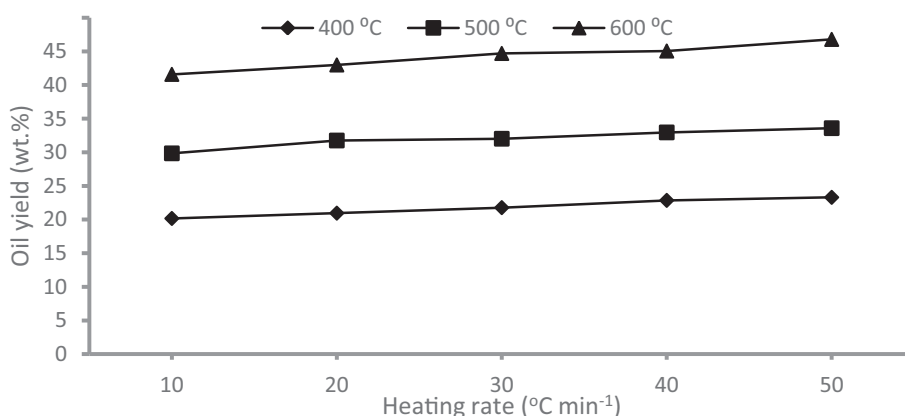|	
Proximate analysis (wt%)	
Moisture	13.21
Volatile matter	7.26
Ash	4.80
Fixed carbon	74.73
Ultimate analysis (wt%)	
Carbon	48.20
Hydrogen	5.40
Nitrogen	1.60
Sulphur	0.80
Oxygen	44.00
Fibre content analysis (wt%)	
Lignin	26.40
Cellulose	33.30
Unicellulose	30.10
Extractives	10.20

Fig. 2. Effect of heating rate on product yield for non-catalytic pyrolysis.

to 52.86 wt% and the bio-oil yield increased from 20.16 to 23.30 wt %. The decrease in char and increase in bio-oil yield with increasing heating rate was attributed either to greater primary decomposition of biomass at higher heating rate or secondary decomposition of the char [20]. The increase in gas products from 20.79 to 23.84 wt% was thought to be predominantly due to the secondary cracking of the pyrolysis vapour at higher heating rate. The secondary decomposition of char at higher heating rate may also give some non-condensable gaseous products, which also contributes to increase in the gas yield [21]. Similar trends were observed for constant temperatures of 500 and 600 °C; at 500 °C, the char decreased from 46.20 to 40.02 wt%, the bio-oil and the gas increased from 29.84 to 33.58 wt% and 23.96 to 26.40 wt% respectively. Also at 600 °C, the char decreased from 32.87 to 26.05 wt%, the bio-oil and the gas increased from 41.58 to 46.78 wt% and 25.55 to 27.17 wt% respectively with the increase in heating rate. These results showed that the maximum yield of the bio-oil was obtained at the heating rate of 50 °C/min for the three constant studied temperatures of 400, 500 and 600 °C.

3.3. Effect of temperature on product yield for non-catalytic pyrolysis

The impact of pyrolysis temperature on products yield is shown in Fig. 3. The pyrolysis experiments were performed at the various temperatures of 400–600 °C with 50 °C intervals. The oil yield was 23.29 wt% at the pyrolysis temperature of 400 °C and attended a maximum yield of 45.67 wt% at 600 °C. Greater primary decomposition of biomass and secondary decomposition of char as the temperature increased may have enhanced the bio-oil yield [22]. The amount of char was found to be decreasing with the increase in pyrolysis temperature while the gaseous products increased with temperature. This observation is similar to the research of Xuel et al. [23], who reported decrease of the bio-char as the pyrolysis temperature was increased. The observed bio-oil yield increment with corresponding temperature raise is similar to investigation on catalytic (HZSM-5) biomass pyrolysis between 400 and 600 °C in a fixed-bed which was found to favour the production of bio-oil and gaseous products at higher temperature [24].

3.4. Effect of catalyst loading on product yield for catalytic pyrolysis at constant temperature of 600 °C

Catalytic pyrolysis experiments were carried out at catalyst to biomass ratio of 0.05–0.25 to examine the impact of catalyst loading on pyrolysis products yield as shown in Fig. 4. The bio-oil yield without catalyst at pyrolysis temperature of 600 °C was 45.67 wt% and reached the maximum yield of 40.83 wt% with catalyst/biomass ratio of 0.05. Both the bio-oil and char decreased with the increase of catalyst amount. The maximum gas product yield was 28.77 wt% for catalytic pyrolysis and 22.91 wt% for non-catalytic pyrolysis which was attributed to further decomposition of bio-oil with the increase in catalyst dosage. This observation is similar to the report of Sadaka and Boateng [25] who worked on slow pyrolysis using HZSM-5 catalyst. The result also indicated that the bio-oil yield decreased while the gas product yield increased as the catalyst/feed ratio increased.
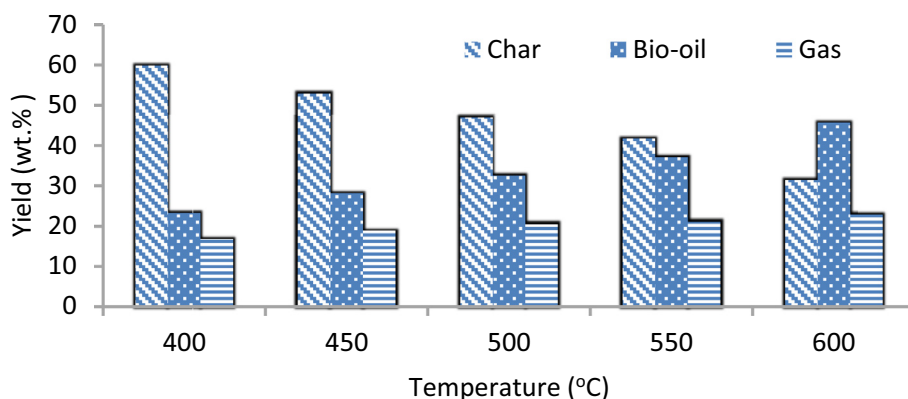

Fig. 3. Effect of temperature on product yield from non-catalytic pyrolysis (at constant 40 mL/min, 50 °C/min and 10 min).
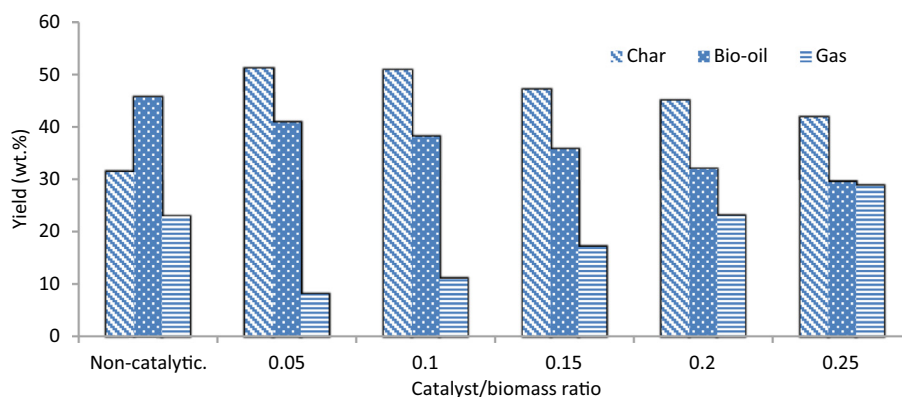

Fig. 4. Effect of catalyst loading on product yield for catalytic pyrolysis at constant temperature of 600 °C.

3.5. The FT-IR results for the maximum yields of non-catalyzed and catalyzed bio-oils

The FTIR spectra of the catalyzed bio-oil (Figure not shown) but presented in data in Table 2. The result showed that the O—H stretching vibrations between 3500 and 3400 cm^{-1} is an indication of the presence of phenols. The functional groups and the corresponding peaks of non-catalytic and catalytic pyrolysis bio-oils are also shown in Fig. 5. The broad absorption band between 3350 and 3200 cm^{-1} of C—O stretching indicated the presence of alcohols. The presence of alkanes is indicated by the absorbance peak of C—H vibrations between 3000 and 2800 cm^{-1}. The peak of C=O vibrations between 1760 and 1665 cm^{-1} indicate the presence of ketones, aldehydes and esters and carboxylic acid. The same functional groups present in non-catalytic oil (Table 2), are also found in catalytic oil except that the amount of oxygenated compounds decreased and saturated hydrocarbon increased in catalytic oil. The C—C stretching vibrations with absorbance 1550–1550 cm^{-1} indicate the presence of aromatics. The decrease in the oxygenated compounds is an indication of secondary reactions in which oxygen is removed in the form of water vapour, CO$_2$ and CO as a result of dehydration and decarboxylation reactions [26].

The presence of aromatics is assigned to the good acid catalyzed aromatization ability of HZSM-5 [27].

The optimum conditions obtained using user-defined response surface methodology in the Design expert software for maximum bio-oil yield are summarized on Table 3. Subsequent analyses of the bio-oil were carried with bio-oil produced at these conditions.

3.6. The GC–MS results for the maximum yields of non-catalyzed and catalyzed bio-oils

The chemical composition of the bio-oil was analyzed using GC–MS. The GC–MS analysis was focused on similar components present in both catalytic and non-catalytic pyrolysis bio-oils for comparison. The two important quantitative data generated from GC–MS analysis are the peak area and retention time which are presented in Table 4.

The results revealed that there was significant difference between the non-catalytic and catalytic pyrolysis GC–MS length of time between the bio-oil injection and elution of individual components or the target compounds peak (retention time); also the amount of electronic charge measured over a certain period by the detector (peak area). The main compounds identified were phenolic compounds and their derivatives which were approximately 19.26% and 29.63% for non-catalytic and catalytic bio-oils products respectively. The detected oleic acid, 9-octadecenoic acid C$_{18}$H$_{24}$O$_2$ with 18 carbon atoms which had peak area of 41.88% in non-catalytic and 7.75% in catalytic pyrolysis bio-oils. The presence of acids though could serve as a source for chemical feedstock when harnessed but causes corrosion effects and a hindrance for use in transportation sector which is detrimental to the bio-oil quality [28].

Table 2
FT-IR result of both non catalyzed and catalyzed bio-oil.

Non catalyzed bio-oil		Non catalyzed bio-oil	
Peaks position	Intensity	Peaks position	Intensity
432.07	6.4	386.67	6.354
1080.17	18.149	420.5	4.736
1269.38	17.401	1066.67	16.023
1371.43	17.484	1203.42	15.023
1647.28	14.528	1307.42	14.167
2062.94	20.206	1636.65	12.43
2346.48	18.724	1714.77	12.43
2936.65	16.6	2078.37	12.00
3420.87	16.771	2350.34	22.36
4504.9	14.12	2938.65	13.492
		3466.2	9.734
		4547.51	24.046

Table 3
Summary of the optimum conditions for maximum bio-oil yield.

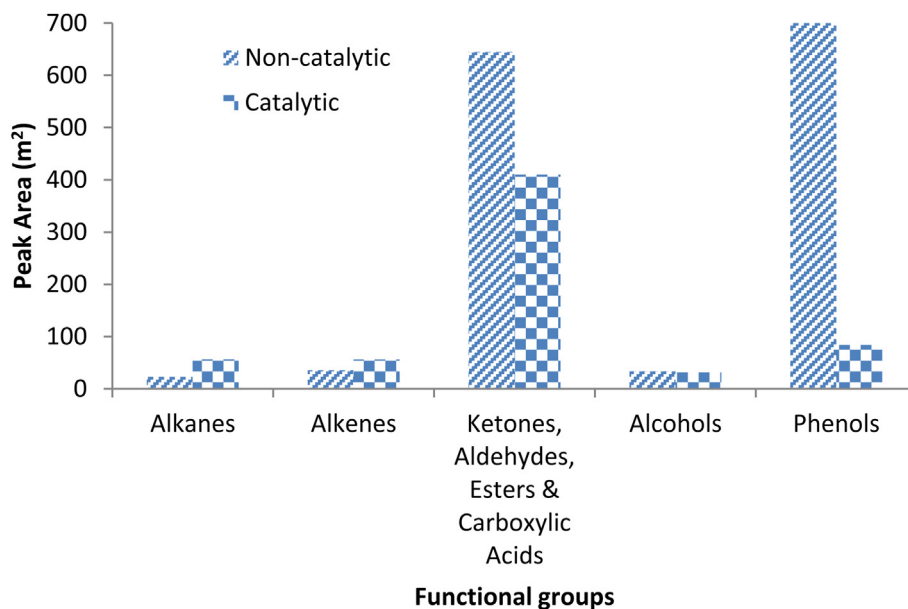| Optimum conditions	Non-catalyzed bio-oil	Catalyzed bio-oil
Heating rate	50 °C/min	50 °C/min
Pyrolysis temperature	600 °C	600 °C
Catalyst/biomass ratio	–	1:20 (0.05)

Fig. 5. FT-IR peaks areas of non-catalytic and catalytic pyrolysis bio-oils.

Table 4
Relative proportion (area %) of similar compounds in bio-oils.

Name of compound	Formula	Peak area (%)		Retention time (min)	
		Non-cat.	Cat.	Non-cat.	Cat.
2-Methylphenol	C_7H_8O	1.838	2.999	5.444	5.189
4-Ethylphenol	$C_8H_{10}O$	7.585	14.601	5.594	5.564
1,2-Cyclopentanedione	$C_5H_6O_2$	1.322	2.649	6.439	5.984
3-Methyl-2-cyclopentenone	C_6H_8O	4.323	6.481	7.960	7.230
Toluene	C_7H_8	0.319	0.363	9.371	8.445
m-Xylene	C_8H_{10}	1.404	2.423	10.601	9.131
2,4-Dimethylphenol	$C_8H_{10}O$	6.020	7.381	12.222	10.471
1,2-Benzenediol	C_6H_6O	0.269	0.477	12.567	11.041
Free sugar	$C_6H_{12}O_6$	0.690	1.342	13.717	11.962
5-Hydroxymethylfurfural	$C_6H_6O_3$	0.430	0.509	15.088	13.072
3-Methylphenol	C_7H_8O	0.410	0.875	17.589	15.078
O-Methoxyphenol	$C_7H_8O_2$	1.220	1.257	18.479	15.798
2,6-Dimethoxyphenol	$C_8H_{10}O_3$	0.558	0.694	19.068	17.531
4-Ethyl-2-methoxyphenol	$C_9H_{12}O_2$	1.629	1.821	21.423	18.347
Oleic acid	$C_{18}H_{24}O_2$	41.885	7.756	35.111	25.612
Total area		69.902	49.677		

Non-cat. = non-catalyzed, Cat. = catalyzed.

4. Conclusion

Pyrolysis using HZSM-5 zeolite catalyst of sugarcane bagasse in a fixed-bed reactor was investigated to improve some properties of bio-oil in terms of the acidity, viscosity, water content and heating values. The fixed-bed operating factors such as heating rate, pyrolysis temperature and catalyst/biomass ratio impact on the product (bio-oil) was significant. The non-catalytic pyrolysis gave the maximum percentage yield (45.67 wt%) of bio-oil at a pyrolysis temperature of 600 °C, heating rate of 50 °C/min, sweeping gas flow rate of 40 mL/min, catalyst/biomass ratio of 0.05 and the catalytic pyrolysis gave (40.83 wt%) of bio-oil at the same conditions. The FT-IR analysis (revealing functional groups) showed that the non-catalytic bio-oil was dominated by oxygenated compounds, while the catalytic bio-oil is dominated by desirable compounds. The chemical composition present in the bio-oil was analyzed using GC–MS which revealed higher percentage of desirable phenolic compounds and lower undesirable acidic groups when compared with the non-catalyzed pyrolysis bio-oil. This study has confirmed the assertion that catalytic pyrolysis can significantly improve the fuel properties of bio-oil in the presence of some requisite selected catalyst.

Acknowledgements

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