Original Article *Journal of Sustainability and Environmental Management (JOSEM), Vol. 1, No. 2 (2022), 120 – 128*
p-ISSN 2822-1729, e-ISSN 2822-1737 Available online at https://www.nepjol.info/index.php/josem

Properties of Upgraded Bio-oil from Pyrolysis of Waste Corn Cobs

Michael Terungwa Abatyough[1,2*], Victor Olatunji Ajibola[2], Edith Bolanle Agbaji[2], Zakka Israila Yashim[2]

[1]Bingham University, Karu, Nigeria
[2]Ahmadu Bello University, Zaria, Nigeria

**Corresponding author: abatyough.michael@bhu.edu.ng*

Abstract: Technologies for conversion of waste solid materials to liquid fuel and bio-crude oil have been researched widely for the production of renewable energy as substitute to fossil fuel oil. However, ash composition of biomass affects the pyrolysis process and the bio-crude oil product has unsatisfactory properties compared to conventional petroleum oil, such as, low heating value, high viscosity, corrosiveness, and the presence of oxygenated compound which causes bio oil ageing. This paper investigated the total waste materials; corn cobs and paper sludge obtained in municipal areas of Abuja, Nigeria, employed in pyrolysis of demineralized corn cobs and the upgrade of crude bio oil via thermal cracking using zeolite prepared from waste paper sludge, with expectation to improve bio oil properties. Demineralization of corn cob removed most of the ash content of biomass allowing for pyrolysis process. The prepared zeolite with mesoporous cage-like crystals analyzed using SEM was able to effectively catalyze thermal cracking of the crude bio oil and reduce the quantity of less desired high molecular weight oxygenated compounds. The bio oil chemical composition obtained from GC-MS analysis indicated the bio oil consisted of oxygenated compounds and hydrocarbons such as aliphatic hydrocarbons (28.768%), alcohols (-0.001%), amines (10.472%), carboxylic acids (0.144), phenols (0.047%), and esters (60.57 %), which significantly influenced the bio oil properties. The physical and chemical properties of the corn cob bio oil was determined for density (0.852 ± 0.03), viscosity (1.66 ± 0.01), cloud point (-34.0 ± 0.02) and calorific value (30.9 ± 0.01). With the exception of Flash point (58 ± 0.01) and acid value (13.1 ± 0.03). In comparison, the produced bio oil had properties likened to petroleum fraction of conventional gasoline than diesel. In conclusion, pyrolysis of corn cob and upgrade of the crude bio oil using prepared zeolite was found as a promising process in improving bio oil quality. The pyrolysis study has potential in the management of environmental wastes to help resolve the challenge of solid waste disposal.

Keywords: *Biomass, Bio-oil, Environmental waste materials, Gasoline fuel, Pyrolysis, Zeolite*

Conflicts of interest: None
Supporting agencies: None

Received 08.04.2022; Revised 03.05.2022; Accepted 11.05.2022

Cite This Article: Abatyough, M.T., Ajibola, V.O., Agbaji, E.B. & Yashim, Z.I. (2022). Properties of Upgraded Bio-oil from Pyrolysis of Waste Corn Cobs. *Journal of Sustainability and Environmental Management*, 1(2), 120-128.

1. Introduction

Biomass is a renewable energy source that can be utilized to manufacture a wide range of chemicals and products (Bridgewater and Grassi, 1991; Chum and Overend, 2001; Sun et al., 2021). Biomass has a number of advantages over conventional fossil fuels, including their minimal sulfur and nitrogen content, as well as no net CO2 emissions into the atmosphere (Bridgewater and Grassi, 1991; Yang et al., 2015). Biomass is referred to as organic matter that is derived from living things and is available as a renewable and sustainable resource. It is made up mostly of carbon, hydrogen, oxygen, nitrogen, and a trace amount of sulfur (Capunitan and Capareda, 2012). Forest products, energy crops, agricultural waste and waste by-products, residues from various industrial activities such as pulp and paper mills, sawmills, and the organic part of industrial and municipal trash are all examples of biomass resources. (Bar-On et al., 2018). Lignin, hemicellulose, cellulose, extractives, and inorganic components make up biomass composition.

Biomass is the world's fourth largest source of energy, accounting for 12% of total primary energy production globally; in many developing nations, such as those in Africa, it accounts for 40-50% of total energy production (Trinh et al., 2013; Cordella et al., 2013). Large volumes of agricultural left overs are presently used as raw material for the paper industry or as animal feed sources in developing nations like Nigeria. . In Nigeria, around 1.5 million tons of corncobs were collected out of a total corn yield of over 7 million tons recorded in 2010 (Suberu et al., 2012). However, when collection and disposal of these residues become increasingly difficult and expensive, they are often discarded as waste or simply burned in the fields, causing considerable environmental problems. Physical, biological, chemical, or thermal conversion processes can be used to create a solid, liquid, or gaseous fuel from biomass. Thermochemical conversion seems to be the most promising method for producing bio oils and other valuable compounds. Biomass pyrolysis is one of the most efficient biofuel production technologies and pyrolysis has proven to be an excellent technique for increasing the value of biomass, these may be done on practically any biomass source. The process involves heating biomass polymers in the absence of oxygen which allows them to depolymerize but inhibits burning (Lopez et al., 2017). Pyrolysis is divided into two types: fast pyrolysis and slow pyrolysis. Slow pyrolysis is considered more in this study. Slow pyrolysis produces roughly 35 wt. % charcoal, 30 wt. % liquid, and 35 wt. % gas by gently heating biomass feedstock to 450-500 °C, with vapour residence times ranging from minutes to hours. Bio char is usually the principal product produced from this process. (Ravikumar et al., 2017). Bio-oil produced from biomass pyrolysis is environmentally benign because it emits the least amount of greenhouse gases. However, its fuel qualities remain unsatisfactory and requires the crude bio oil to be upgraded in order to compare to fossil fuels, particularly in terms of combustion efficiency. Several methods such as esterification, hydrogenation, thermal cracking, fractionation, and other processes are used to upgrade these bio-oils and improve their characteristics for various uses (Chan et al., 2020). Heavy molecular weight compounds will condense first while water and other light oxygenates remain in the vapour phase, allowing bio-oil fractionation to separate water- and water-soluble chemicals such as organic acids (Zhang et al., 2013; Mei et al., 2019; Sun et al., 2021). Physical and chemical properties such as water content, oxygen content, ash content, viscosity, density, calorific value, acidity/pH, and the chemical makeup affect utilization of bio-oil as fuel and other applications. Biomass is majorly obtained as environmental wastes and its constituents, which vary with various biomass species are known to influence the properties, composition and amount of pyrolysis products. (Raveendran, et al., 1996; Yang et al., 2015). Osayi and Osifo (2019) and Miandad et al., (2016), reported the use of prepared zeolites zeolite for improved properties of pyrolytic oil and attributed the findings to structural properties of the catalyst used. This enabled the use of other catalysts to be investigated. Catalytic pyrolysis is an effective process of bio oil production and waste management. Several research on pyrolysis of biomass exists, nevertheless, according to literature and knowledge available to the author, no study has focused on the application total waste materials in preparation of zeolite using waste paper sludge as a precursor and its application in slow pyrolysis of demineralized waste corn cobs biomass. The liquid bio oil produced will be characterized for its chemical composition using GC– MS technique and physicochemical properties to determine its fuel suitability. The aim of this research was to investigate the slow pyrolysis of waste corn cob biomass using prepared zeolite catalyst obtained from waste paper sludge. The experiments were carried out in laboratory scale batch reactor and in-situ upgrading for enhanced bio oil properties. The study will be relevant in valorization and management of wastes.

2. Materials and methods

Waste materials, corn cobs and paper sludge were collected from municipal areas around Abuja in Nigeria. The corn cobs were sundried to reduce moisture before milling to microscopic particle sizes. Waste paper sludge was also collected and washed using distilled water before drying in the oven, it was calcined for 8 hours at 550°C. The paper sludge-ash was collected and stored.

2.1. Demineralization of corn cob

The demineralization process was carried out to reduce the amounts of ash, alkali and alkali earth metals. The prepared waste corn cob biomass 5g, was washed with 50 cm3 of nitric acid solvent for one hour at room temperature and left overnight. The solvent was discarded and a fresh amount was added, this process was repeated consecutively for three days and the residue rinsed with distilled water. The residue was oven dried at 1100c for one hour.

2.2. Characterization of waste corn cobs

American Society for Testing and Materials standard methods were used in characterization of the waste corn cobs. Moisture content, ash content, and volatile matter of corn cobs were determined using the methods; ASTM E1756-01, ASTM E1755-01, and ASTM E872-82. The dry weight percentage was used to represent the average results from the sample. The percentage of fixed carbon was calculated from amounts of volatile matter (VM) and ash content (AC) using the following formula:

$$\text{Fixed carbon (wt.\%)} = 100 - (VM + AC) \quad (1)$$

2.3. Experimental set-up

A 100 g of corn cob was placed in a quartz flask. Pyrolysis reactions were carried out in nitrogen atmosphere using an electric heating mantle. Thermocouple was put in the middle of the feedstock mass and connected with the electric heating mantle to control the pyrolysis temperature. A heat exchanger condenser consisting of a low-temperature thermostatic bath was used to collect volatile vapor phase products in a collecting bottle. Equation 2 was used to calculate the bio oil yield.

$$\text{Bio} - \text{oil yield} = \frac{\text{Weight of bio-oil}}{\text{Weight of (corn-cob)}} X\, 100 \qquad (2)$$

2.4. Characterization of Bio-oil

The separation and identification of all the compounds present in the crude bio-oil was performed using a gas chromatograph mass spectrometer (GC-MS). The upgraded bio-oil was analyzed for the properties; density (ASTM D4052) and viscosity (EN 16896), acid value (ASTM – D 974(00), calorific value and cloud point according to standards. (ASTM 2006; ASTM 2007).

3. Results and discussion

3.1. Physicochemical properties

Table 1 shows the results of proximate and elemental analyses of the corn cob biomass. The thermal composition parameters and biomass fuel quality are determined by proximate analysis (Varma and Mondal, 2017). The quality and amount of pyrolysis liquid are affected by the volatile matter and ash concentration. The mineral content (ash) of biomass can have a big impact on the pyrolysis process, it is also known to deactivate the catalyst in catalytic pyrolysis (Jiang et al., 2020). The corn cob ash concentration was found to be 1.05 wt. %. This is within acceptable limits, but it also suggests that alkali and alkali earth-metals may be present in biomass, this suggests the biomass be demineralized prior to pyrolysis. According to Jiang et al., (2020). Microwave-assisted glycerol pretreatment favored demineralization and delignification. Owing to demineralization, delignification, and concentration of crystalline cellulose via pretreatment, the yield of levoglucosan (44.5%) was significantly increased as compared to that of un-pretreated corncobs (6.9%) in fast pyrolysis. Vassilev et al., (2013), also reported on the composition and application of biomass ash, they concluded that pretreatment methods such as demineralization to be effective in improving yields. Although small levels of moisture in biomass may improve the condensation of volatile components like bio-oil from steam, moisture content has a propensity to affect biomass during storage. The moisture content of corn cobs was found to be 7.14 wt. %. For the pyrolysis process, this is okay. Kim et al., (2016) reported similar low moisture contents in cellulose feedstock pyrolysis over zeolites. Moisture content should be less than 11% for the pyrolysis process, according to Bridgwater et al., (1999). The volatile content of the corn cobs was determined to be 87.1 wt%. A biomass material with higher volatile content was easily devolatilized and more reactive than lower volatiles containing biomass Graboski and Bain, (1981). The amount of bio-char that can be obtained from the pyrolysis process is called fixed carbon of biomass, and it can affect the bio-oil production (Li et al., 2021). The fixed carbon for corn-cobs was determined as 11.25 wt. %. The corn cob feedstock contained 43.58 wt. % carbon, 6.44 wt. % hydrogen, 0.67 wt. % nitrogen, 0.001 wt. % sulfur, and 49.30 wt. % oxygen, according to the elemental analysis. Because the corn cob feedstock has a low amount of nitrogen and sulfur, the findings of elemental analysis indicate that the corn cob biomass is environmentally safe to use as a feedstock for the pyrolysis process. As a result, the combustion products of their bio-oil would be influenced (Diallo et al., 2021). The high carbon content would improve the calorific value of its products.

SEM micrographs for prepared zeolite from waste paper sludge at two magnifications 30.0 Kx and 10.0 Kx is shown in Figure 1. It shows a highly mesoporous flake-like crystal network is observed, in general the prepared zeolites possess characteristic surfaces of the faujasites type, a mesoporous network of cage-like crystals with large pore spaces between them (Kaduk, 2005). Similar images were obtained by Zhao et al., (2016) where Mesoporous zeolite-Y (denoted as meso-Y) was synthesized using hydrothermal synthesis method, they reported them to have high micro-activity and lowest coke yield this was ascribed to the mesoporous structure which is known to improve the mass transfer of the larger molecules. Also a study by Tang et al., (2017) showed that zeolite-Y nanoparticle assemblies (Y-NA) with a mesoporous structure were directly synthesized at 75 °C for 16 hours. The results showed that Y-NA had a micro–mesoporous structure composed of highly crystalline particle assemblies with sizes of 400–900 nm. TEM micrographs are shown in Figure 2, for the prepared zeolite from waste paper sludge. The images show a highly porous poly-crystalline network of crystals of varying shapes and sizes. This is characteristic of highly porous zeolite crystals.

3.2. Compounds distribution

One of the key elements that renders bio-oil non-useful is its chemical composition. Table 2 shows the detected chemicals and their distribution as area % resulting from the GC-MS study. Small chromatogram peaks, as well as peaks belonging to undetermined chemicals, are not included in the table. The chromatogram for bio-oil derived from slow pyrolyzed corn-cob is given in Figure 3. A complicated mixture of water and organic compounds made up 99.0 % of the bio-oil generated by pyrolysis. The chemical composition of the bio-oil consisted of oxygenated compounds and hydrocarbons such as aliphatic hydrocarbons (28.768%), alcohols (-0.001%), amines (10.472%), carboxylic acids (0.144), phenols (0.047%), and esters (60.57 %). 2,4-Di-tert-butylphenol, Hexadecane, 2,6,10-trimethyl-, Pyridine, 3,5-diethoxy-, 1-oxide, Dodecanoic acid, Dodecanoic acid, 1,2,3-propanetriyl ester, and others were among the major chemicals discovered. Various investigations have found comparable chemicals in biomass-derived bio-oils. Khuenkaeo and Tippayawong (2020) reported that major organic compounds found in corncob oil were phenolic compounds including: 1,2-benzendiol, phenol 4 ethyl, phenol 2,6-dimethoxy, and phenol 4-ethyl-2-methoxy that percentage of area were about 18, 11, 10, and 9, respectively. In addition, aromatic compound, benzene 1-3-dimethyl-2 propoxy was significantly high, area % as 12. Biswas et al., (2017) studied pyrolysis of agricultural biomass residues (corn cob, wheat straw, rice straw and rice husk). They reported that all bio-oils contents were mainly composed of oxygenated hydrocarbons. The higher area percentages of phenolic compounds were observed in the corn cob bio-oil than other bio-oils. Similar compositions were also reported by Tsai et al., (2006) and Chen et al., (2011) for bio oil production from rice husk. The large number of hydrocarbons found in the bio-oil indicates that it can be used as a bio-fuel. It also indicates that deoxygenation will boost its storage capabilities.

3.3. Physicochemical properties of bio oil

The bio oil obtained from corn cob pyrolysis was employed in the determination of some physicochemical properties of corn-cob bio-oil, a summary of the results and their comparison between two types of conventional fuels; gasoline and diesel is shown Table 3. This comparison will indicate the suitability of the corn cob bio oil as a fuel. The liquid products, commonly referred to as crude bio-oil, are usually reddish-brown in color and have an unpleasant odour. (Prasertpong et al., 2017). The bio oil in this study was upgraded via distillation to obtain a clear liquid product. The composition of bio-oil has a considerable impact on the characteristics as well as its storage and application, the ageing and energy value of bio oil is also affected by the density and viscosity. (Hassan et al., 2020; Fekhar et al., 2020). The bio oil in this study had a density of 0.852 ± 0.03 g/cm3 and a viscosity of 1.66 ± 0.01 cst. The determined density is higher than gasoline standard of 0.715–0.780, but within the range for diesel standard 0.845 - 0.860. These values are attributed to the chemical composition of the bio oil. Fekhar et al., (2020), reported that the presence of large amount of high molecular weight oxygenated compounds in the bio oil increases the density and viscosity. Varma and Mondal (2017), reported high density up to 1.039 g/cm3 and viscosity up to 27.0 cst for pyrolysis of cellulose with plastics. Ingram et al., (2008) also reported density of 1.19 g/cm3 and viscosity of 5.3 Cst, for Pyrolysis of wood and bark. The acidity of bio oil is not a desirable quality due to its ageing effect and eventual corrosion of operating equipment (Van Nguyen et al., 2019). The acid value of bio-oil was determined as 13.1 ± 0.03 mgKOH, this is higher than the values for both conventional gasoline <1, and diesel 0.08 – 1.0. The acidity of the bio oil is attributed to the presence of carboxylic and phenolic acids. Acid values as high as 20 mgKOH were reported by Fekhar et al., (2020) for pyrolysis of paper and plastics, these values increased even more with age. Varma and Mondal (2017), also reported acidity in bio oil from pyrolysis of sugarcane bagasse, with pH ranging from 2.0 – 6.0. Christensen et al., (2013) studied the titration of hydrotreated biomass and reported high acidity in bio oil with pH up to 16.0, this was attributed to the presence of large amounts of carboxylic and phenolic chemicals. When a liquid is exposed to a flame, the flash point is the lowest temperature at which the vapor above the liquid will ignite. The flash point of bio-oil was determined to be 58 ± 0.01 oC, this value is higher than conventional gasoline and diesel specifications but is much closer to diesel. Varma and Mondal (2017), recorded flash points ranging from 63 – 107 oC for pyrolysis of sugarcane bagasse. In terms of volatility, the flash point of bio-oils has an impact on their use as a fuel (Idris et al., 2020). The flash point is related to the bio oil viscosity and density. The molecular weights of the components in bio-oils will have a big impact on the cloud point. (Hossain and colleagues, 2019). The greatest temperature at which a cloud of waxy crystals becomes visible is called cloud point. The bio-oil became cloudy at -34.0 ± 0.02 oC. The carbon content of bio oil is proportional to the heating value. A calorific value of 30.9 ± 0.01 MJ/kg was determined in the bio oil, which is lower than both conventional gasoline 44–46 MJ/kg, and diesel 43.06 MJ/kg, specifications. The calorific value is indicative of the hydrogen to carbon ratio. According to Khuenkaeo and Tippayawong (2020), the calorific value of bio-oils derived from various biomass was around 25.3 MJ/kg for pyrolysis of coconut shells, 20.4 MJ/kg for bamboo, and 20.0 MJ/kg for corncobs, respectively. Similarly, in varied experimental conditions, Ling et al., (2015) reported calorific values averaging 30.0 MJ/kg for bio oil from pyrolysis of oil palm biomass. Calorific values up to 43 MJ/kg were recorded by Varma and Mondal (2017). The high energy value reflects the amount of carbon to hydrogen ratio in the bio-oil.

Table 1: Physicochemical properties of corn-cob

Feedstock	**Corn-cob**
	Proximate analysis (wt. %)
Moisture	7.14
Ash content	1.05
Volatiles	87.7
Fixed carbon	11.25
	Elemental analysis (wt. %)
C	43.58

H	6.44
N	0.67
O	49.30
S	0.001

Table 2: GC-MS profile of corn-cob feedstock

RT	Compound	Area %
10.5455	2,4-Di-tert-butylphenol	0.047
31.1745	1-Azabicyclo[2.2.2]octan-4-ol	-0.0054
42.9335	Tetradecane, 3-methyl-	8.1552
45.138	Pentadecane, 6-methyl-	5.2895
43.639	Hexadecane, 2,6,10-trimethyl-	19.0031
42.285	Octanoyl chloride	1.3727
24.4431	5-Eicosene, (E)-	0.2379
39.1868	Eicosanoic acid, heptyl ester	0.2035
32.3718	Pyridine, 3,5-diethoxy-, 1-oxide	7.5639
41.4115	1,3,5-Triazin-2(1H)-one, 4,6-bis(ethylamino)-	0.8204
11.9896	Dodecanoic acid	0.1442
35.741	Acetic acid, 6-iodo-9-oxabicyclo[3.3.1]non-2-yl ester	0.3212
33.0498	Dodecanoic acid, 2,3-dihydroxypropyl ester	1.3294
51.8238	Methoxyacetic acid, tetradecyl ester	0.0575
50.9032	Dodecanoic acid, ethenyl ester	0.2728
46.7487	Dodecanoic acid, 1,2,3-propanetriyl ester	58.5921

Table 3: Properties of bio-oil

Property	Corn cob bio-oil	Conventional fuel	
		Gasoline	Diesel
Density(15^0C) (g/cm^3)	0.852 ± 0.03	0.715–0.780	0.845 - 0.860
Viscosity (40^0C) (Cst)	1.66 ± 0.01	0.40–0.75	4.0 - 4.5
Acid value (mgKOH)	13.1 ± 0.03	<1	0.08 – 1.0
Flash point (^{0}C)	58 ± 0.01	28 ^{0}C	55 ^{0}C
Cloud point (^{0}C)	-34.0 ± 0.02	-	-
Calorific value (MJ/kg)	30.9 ± 0.01	44–46	43.06

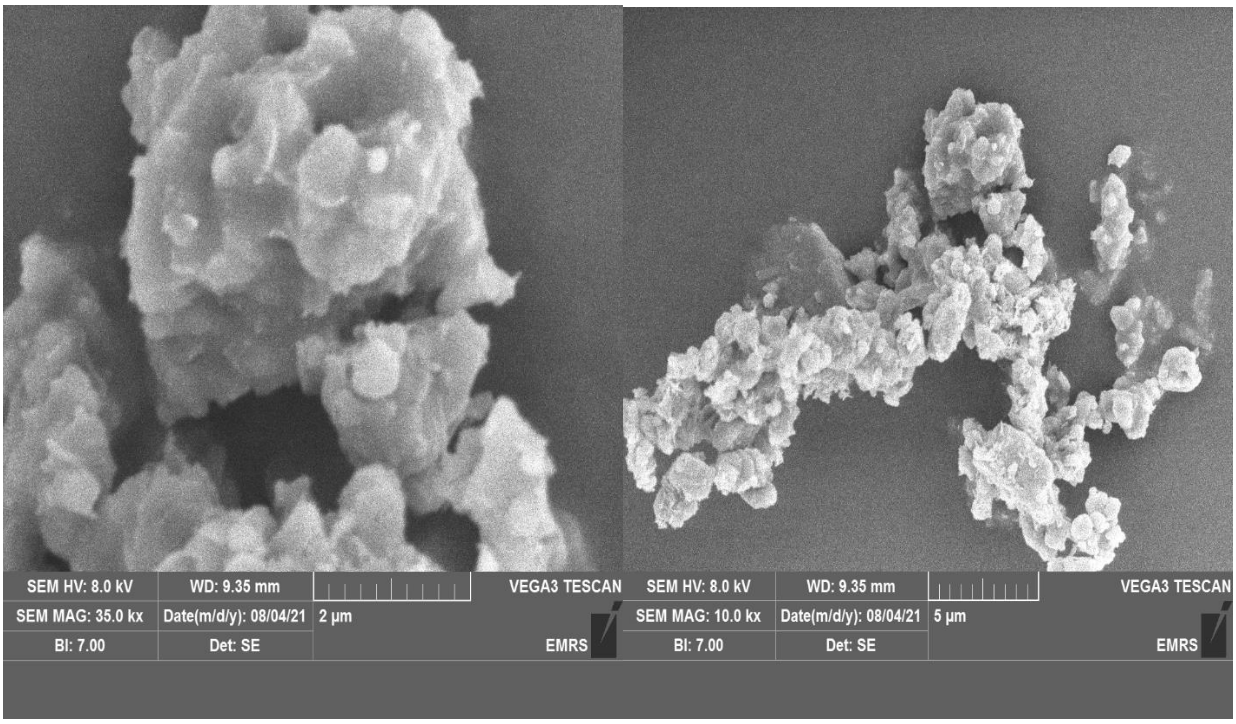

Figure 1: SEM micrographs of zeolite at 10.0KX and 35.0 KX magnifications

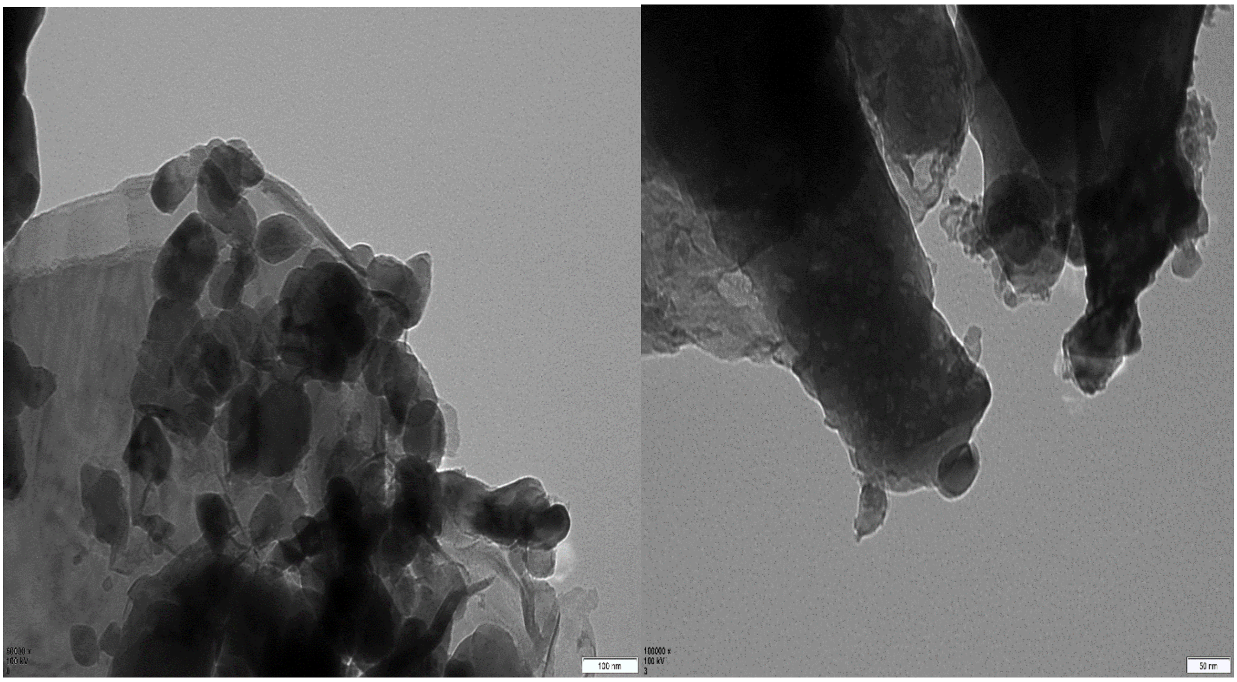

Figure 2: TEM micrographs of zeolite at 100nm and 50nm.

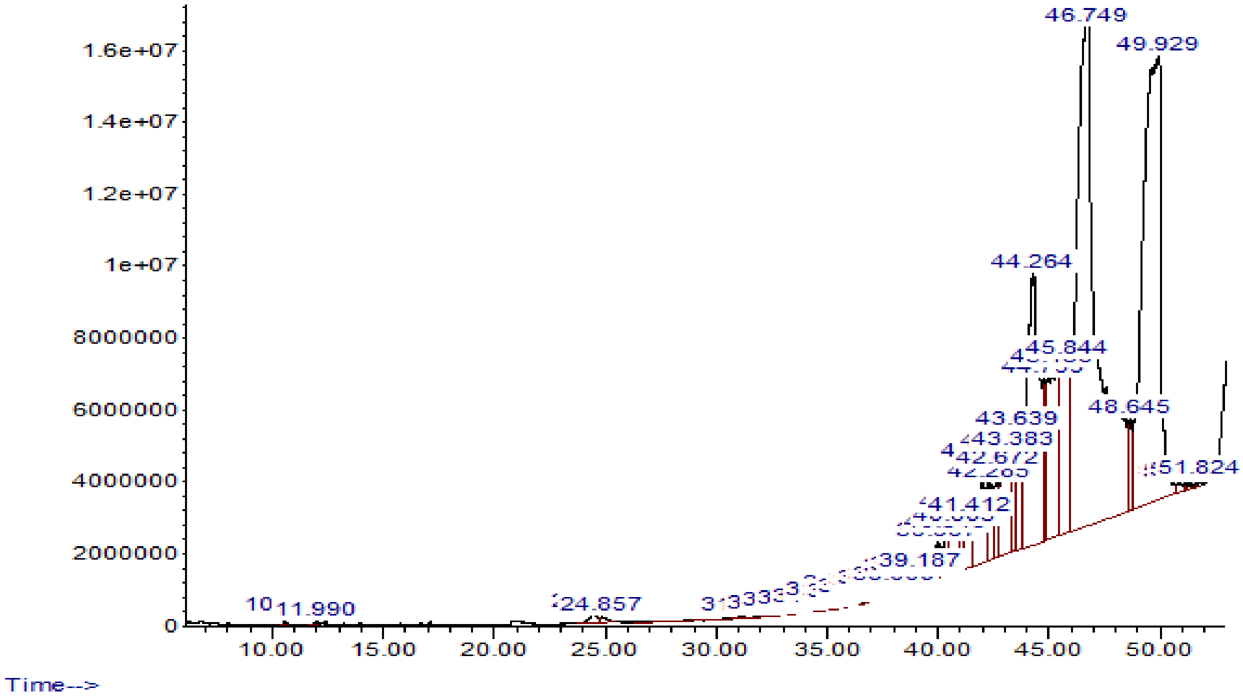

Figure 3: GC-MS Chromatogram of bio-oil

4. Conclusion

The management of environmental solid waste materials, biomass, and their utilization in technologies for conversion to sustainable liquid biofuel has been problematic due to the high mineral content in biomass affects the pyrolysis process and the pyrolysis product crude bio oil has unsatisfactory properties attributed to presence of unwanted oxygenated compounds in the crude bio oil. This paper focusses on the properties of bio oil obtained from pyrolysis of demineralized corn cobs and the crude bio oil upgrade using zeolite catalyzed thermal cracking. Demineralization favoured the pyrolysis process by reducing the ash content of biomass. The prepared zeolite catalyst was able to effectively catalyze thermal cracking of the crude bio oil and reduce less desired high molecular weight oxygenated compounds. The bio oil chemical composition consisted of oxygenated compounds and hydrocarbons such as aliphatic hydrocarbons (28.768%), alcohols (-0.001%), amines (10.472%), carboxylic acids (0.144), phenols (0.047%), and esters (60.57 %) which significantly influenced the bio oil properties. The physical and chemical properties of the corn cob bio oil was determined for density (0.852 ± 0.03), viscosity (1.66 ± 0.01), cloud point (-34.0 ± 0.02) and calorific value (30.9 ± 0.01). With the exception of Flash point (58 ± 0.01) and acid value (13.1 ± 0.03), The results have proved that pyrolysis using waste materials corn cob and paper sludge can produce bio oil with substantially improved properties likened to petroleum fraction of conventional gasoline. Further research can be carried out on co pyrolysis of corn cob with plastics to improve the energy value of the bio oil. This study has potential for production of sustainable fuel and management of environmental waste.

Acknowledgements

The authors gratefully acknowledge the Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria, for the research opportunity.

References

American Society of Testing and Materials (ASTM). (2006). *ASTM E871-82 standard test method for moisture analysis of particulate wood fuels.* New York: ASTM International.

ASTM. (2006). *ASTM E872-82 standard test method for volatile matter in the analysis of particulate wood fuels.* New York: ASTM International.

ASTM. (2007). *ASTM E1755-01 standard test method for ash in biomass.* New York: ASTM International.

Bar-On, Y. M., Phillips, R., and Milo, R. (2018). *80x. Sciences.*

Biswas, B., Pandey, N., Bisht, Y., Singh, R., Kumar, J., and Bhaskar, T. (2017). Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk. *Bioresource Technology*, 237, 57-63.

Bridgwater, T., Czernik, S., Diebold, J., Meier, D., Oasmaa, A., Peackocke, C., and Radlein, D. (1999). *Fast pyrolysis of biomass: A handbook*. CPL-press, Newbury Berkshire, UK.

Capunitan, J.A, Capareda, S.C. (2012). Assessing the potential for biofuel production of corn stover pyrolysis using a pressurized batch reactor. *Fuel*, 95,563–572.

Chan, Y.H., Loh, S.K., Chin, B.L.F., Yiin, C.L., How, B.S., Cheah, K.W., and Lam, S.S. (2020). Fractionation and extraction of bio-oil for production of greener fuel and value-added chemicals: recent advances and future prospects. *Chemical Engineering Journal*, 397, 125406.

Chen, T., Wu, C., and Liu, R. (2011). Steam reforming of bio-oil from rice husks fast pyrolysis for hydrogen production. *Bioresource Technology*, 102(19), 9236-9240.

Christensen, E., Alleman, T., and McCormick, R. (2013). Totalacid value titration of hydrotreated biomass fast pyrolysis oil: Determination of carboxylic acids and phenolics with multiple end point detection. *Papers of the American Chemical Society*, 245.

Chum, H. L., and Overend, R. P. (2001). Biomass and renewable fuels. *Fuel Processing Technology, 71(*1-3), 187-195.

Cordella, M., Stramigioli, C., and Santarelli, F. (2013). *A set of coherent indicators for the assessment of the energy profitability of energy systems.*

Diallo, A. D. D., Alam, M. Z., and Mel, M. (2021). Enhancement of the calorific value of em1707pty fruit bunch (efb) by adding municipal solid waste as solid fuel in gasification process. *IIUM Engineering Journal, 22(*2), 10-20.

Fekhar, B., Zsinka, V., and Miskolczi, N. (2020). Thermo-catalytic co-pyrolysis of waste plastic and paper in batch and tubular reactors for in-situ product improvement. *Journal of Environmental Management*, 269, 110741.

Grassi, G., and Bridgewater, A. V. (1991). *Biomass pyrolysis liquids upgrading and utilisation.*

Hassan, H., Lim, J. K., and Hameed, B. H. (2019). Catalytic co-pyrolysis of sugarcane bagasse and waste high-density polyethylene over faujasite-type zeolite. *Bioresource Technology*, 284, 406-414.

Hossain, M. S., Ferdous, J., Islam, M. S., Islam, M. R., Mustafi, N. N., and Haniu, H. (2019). Production of liquid fuel from co-pyrolysis of polythene waste and rice straw. *Energy Procedia*, 160, 116-122.

Idris, R., Chong, C. T., Asik, J. A., and Ani, F. N. (2020). Optimization studies of microwave-induced co-pyrolysis of empty fruit bunches/waste truck tire using response surface methodology. *Journal of Cleaner Production,* 244, 118649.

Ingram, L., Mohan, D., Bricka, M., Steele, P., Strobel, D., Crocker, D., and Pittman Jr, C. U. (2008). Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. *Energy and Fuels, 22(*1), 614-625.

Jiang, L.Q., Wu, Y.X., Wu, N.N., Zhong, H.Q., Zhang, Y.C., Zhao, Z.L., and Zhang, F. (2020). Selective saccharification of microwave-assisted glycerol pretreated corncobs via fast pyrolysis and enzymatic hydrolysis. *Fuel*, 265, 116965.

Kaduk, J. A. (2005). Extraframework species in zeolite Y at nonambient conditions. *Crystallography Reviews, 11(*1), 1-19.

Khuenkaeo, N., and Tippayawong, N. (2020). Production and characterization of bio-oil and biochar from ablative pyrolysis of lignocellulosic biomass residues. *Chemical Engineering Communications, 207(*2), 153-160.

Kim, B. S., Kim, Y. M., Lee, H. W., Jae, J., Kim, D. H., Jung, S. C. and Park, Y. K. (2016). Catalytic copyrolysis of cellulose and thermoplastics over HZSM-5 and HY. *ACS Sustainable Chemistry and Engineering, 4(*3), 1354-1363.

Li, H., Meng, J., Liu, Z., Lan, Y., Yang, X., Huang, Y., and Chen, W. (2021). Effects of biochar on N2O emission in denitrification pathway from paddy soil: A drying incubation study. *Science of The Total Environment*, 787, 147591.

Ling, C., Kyin, E., Hua, L., Chen, L., and Yee, C. (2015). Yield and calorific value of bio oil pyrolysed from oil palm biomass and its relation with solid residence time and process temperature. *Asian Journal of Scientific Research, 8(*3), 351-358.

Lopez, G., Artetxe, M., Amutio, M., Bilbao, J., Olazar, M. (2017). *Thermochemical routes for the valorization of waste polyolefinic*

Mei, Y., Chai, M., Shen, C., Liu, B., and Liu, R. (2019). Effect of methanol addition on properties and aging reaction mechanism of bio-oil during storage. *Fuel*, 244, 499-507.

Miandad, R., Barakat, M.A., Aburiazaiza, A.S., Rehan, M., Nizami, A.S. (2016). Catalytic pyrolysis of plastic waste: a review. *Process Safe Environment,* 102, 822–838.

Osayi, J. I., and Osifo, P. (2019). Utilization of synthesized zeolite for improved properties of pyrolytic oil derived from used tire. *International Journal of Chemical Engineering*.

Prasertpong, P., Jaroenkhasemmeesuk, C., Tippayawong, N., and Thanmongkhon, Y. (2017). Characterization of bio-oils from jatropha residues and mixtures of model compounds. *Chiang Mai University Journal of Natural Sciences, 16(*2), 135-44.

Raveendran, K., Ganesh, A., and Khilar, K. C. (1996). Pyrolysis characteristics of biomass and biomass components. *Fuel, 75(*8), 987-998.

Ravikumar, C., Kumar, P.S., Subhashni, S.K., Tejaswini, P.V., and Varshini, V. (2017). Microwave assisted fast pyrolysis of corn cob, corn stover, saw dust and rice straw: Experimental investigation on bio-oil yield and high heating values. *Sustainable Materials and Technologies,* 11, 19-27.

Suberu, M. Y., Mokhtar, A. S., and Bashir, N. (2012). Renewable power generation opportunity from municipal solid waste: A case study of Lagos metropolis (Nigeria). *Journal of Energy Technologies and Policy, 2(*2), 1-15.

Sun, J., Norouzi, O., and Mašek, O. (2021). A state-of-the-art review on algae pyrolysis for bioenergy and biochar production. *Bioresource Technology*, 126258.

Tang, T., Zhang, L., Dong, H., Fang, Z., Fu, W., Yu, Q., and Tang, T. (2017). Organic template-free synthesis of zeolite Y nanoparticle assemblies and their application in the catalysis of the ritter reaction. *RSC Advances, 7(*13), 7711-7717.

Trinh, T.N., Jensen, P.A., Dam-Johansen, K., Knudsen, N.O., and Sørensen, H.R. (2013). Influence of the pyrolysis temperature on sewage sludge product distribution, bio-oil, and char properties. Energy and *Fuels, 27(*3), 1419-1427.

Tsai, W.T., Lee, M.K., and Chang, D.Y. (2006). Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal of Analytical and Applied Pyrolysis, 76(*12), 230-237.

Varma, A. K., and Mondal, P. (2017). Pyrolysis of sugarcane bagasse in semi batch reactor: Effects of process parameters on product yields and characterization of products. *Industrial Crops and Products*, 95, 704-717.

Vassilev, S.V., Baxter, D., Andersen, L.K., and Vassileva, C.G. (2013). An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification. *Fuel*, 105, 40-76.

Yang, Z., Kumar, A., and Huhnke, R.L. (2015). Review of recent developments to improve storage and transportation stability of bio-oil. *Renewable and Sustainable Energy Reviews*, 50, 859-870.

Zhang, L., Liu, R., Yin, R., and Mei, Y. (2013). Upgrading of bio-oil from biomass fast pyrolysis in China: A review. *Renewable and Sustainable Energy Reviews*, 24, 66-72.

Zhao, J., Wang, G., Qin, L., Li, H., Chen, Y., and Liu, B. (2016). Synthesis and catalytic cracking performance of mesoporous zeolite Y. *Catalysis Communications*, 73, 98-102.

.