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Characterization Of Bio-Oil Yield from Catalytic Pyrolysis OF *Zea mays indentata* Corncob

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ABSTRACT

Pyrolysis and gasification are the most common biomass thermochemical conversion methods used for liquid and gaseous fuel production. In this study, the effect of zinc oxide catalyst on the quality of bio-oil from catalytic pyrolysis of Zea mays indentata corncob in a fixed bed reactor at optimum bio-oil yield conditions was determined. Non-catalytic pyrolysis was carried out in the temperature range of 450 – 600 ^{C} and residence time range of 20 – 35 mins, according to the D-optimal design of Design Expert software (version 13.0.1), to determine the optimum condition for bio-oil yield. Catalytic pyrolysis was carried out at the optimum condition for bio-oil yield with biomass to catalyst (b/c) weight ratios in the range 97.5/2.5 - 90/10, according to the mixture methodology formulation of Design Expert Software (version 13.0.1). Elemental composition and the basic fuel properties of the bio-oils at optimum bio-oil yield conditions, including viscosity, pH value, ash content and flash point, were determined and compared with those of non-catalytic pyrolysis bio-oil. The highest bio-oil yield (44.94 wt.%) from non-catalytic pyrolysis was obtained at the temperature of 550 °C and residence time of 25 minutes. The highest bio-oil yield (37.45 wt.%) from catalytic pyrolysis at the optimum temperature (550 °C) was obtained at a biomass/catalyst ratio of 90/10. Catalytic pyrolysis bio-oils possessed higher carbon and hydrogen at b/c ratios of 96.67/3.33, 92.5/7.5 and 96.67/3.33. but lower oxygen and sulphur at 96.67/3.33, 92.5/7.5 and 90/10 than non-catalytic pyrolysis bio-oil. The use of a catalyst reduced the viscosity, and ash content (at b/c ratios of 96.67/3.33 and 97.5/2.5), and increased the pH value of bio-oils (at b/c ratios of 95/5 and 90/10). Catalytic pyrolysis improves the quality of pyrolysis bio-oil and can be moderately blended with petroleum diesel to power internal combustion engines. This study also showed that corncob has a high potential for biofuel production and could be exploited as an alternative source of biofuel.

INTRODUCTION

The world energy demand is increasing at an exponential rate with the increasing trend of population. The present energy consumption pattern is showing a significant effect on the global economy as well as on the environment (Panwar and Paul, 2021). The major sources of energy include fossil fuels such as natural gas, coal and petroleum. Therefore, the search for alternative sources of renewable, environmentally friendly and sustainable fuels has gained much attention for decades. Biofuel is one of the promising options of renewable energy gaining popularity globally, as it can produce fuel with similar functionality to crude oil (Brown and John 2019). Biofuels are produced from biomass by either thermochemical or biochemical conversion route. Biomass is a general term for non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. The advantages of biomass over fossil fuels are their low sulphur and nitrogen contents and no net emissions of CO_2 to the atmosphere. Forest and agricultural residues, organic wastes, energy crops, biodegradable organic fractions of municipal solid waste and industrial waste are primary biomass resources. Corncob is one of the main crop residues possible to be subjected to thermochemical treatments and then used as a resource to produce green fuel. One viable option to manage the residue from corncob is to thermally convert it via fast pyrolysis in the absence of oxygen into bio-oil, which can be used as liquid fuel or as a feedstock for various chemical production. Pyrolysis is a thermochemical conversion process in the absence of an oxidizing agent and can be regarded as the initial stage of gasification and combustion. Solid char, liquid pyrolysis oil and gas are the main products of biomass pyrolysis. Pyrolysis oil or bio-oil produced from the pyrolysis of biomass has been identified as a potential fuel to replace fossil fuel in many applications if produced and processed properly (Yang *et al.*, 2013; Czernik and Bridgewater, 2004). In many cases, the direct use of bio-oil as a conventional fuel or chemical feedstock presents several challenges due to their high viscosity, poor/low heating value, corrosiveness and instability. To overcome those difficulties, the catalytic upgrading of bio-oil is widely practiced. Catalytic pyrolysis is a promising way to improve bio-oil quality by removing oxygenated compounds, increasing calorific value, lowering viscosity and increasing stability. The use of Zinc oxide (ZnO) as a catalyst has been studied widely. Zhou *et al*. (2013), studied the pyrolysis of rice husk with the addition of ZnO and the results of the study indicated that ZnO improved the bio-oil compositional quality in terms of low-molecular-weight compounds including alkanes, alkenes, styrene and alkyl phenols (thus increasing bio-oil stability) and the pH value of catalytic bio-oil was recorded as 4.35, whereas non -catalytic bio-oil has a pH value of 4.15. Thus, this indicates the effect of ZnO catalyst on the reduction of acidic compounds in bio-oil. Due to the oil yield potential of corncob, it can be used as feedstock for the production of biofuel. This is to ensure the optimum yield of the intended final product. This paper reports the effect of zinc oxide catalysts on the yield and quality of bio-oil obtained by pyrolysis of *Zea mays indentata*.

MATERIALS AND METHODS

Materials

Zea mays indentata corncob was sourced locally in Odo-oba market, Orire Local Government Area, Ogbomoso, Oyo State, Nigeria. Zinc Oxide (ZnO) catalyst was procured from CAVIDEP Chemical Laboratory, Dada Estate, Osogbo, Osun state, Nigeria.

Methods

Feedstock Processing

The sourced *Zea mays indentata* corncob sample was sundried for five days to reduce the moisture content. The dried corncob was then reduced in size using a grinding machine and sieved to obtain a particle size of 1 mm. It was then weighed and sealed in an air-tight bag to prevent moisture absorption or to maintain the moisture content and kept at room temperature before pyrolysis experiments.

Feedstock characterization

Proximate analysis was conducted to evaluate the moisture content, volatile matter, ash content and fixed carbon of corncob. The moisture content, volatile matter, and ash content were assessed using ASTM D 3173, ASTM D 3175 and ASTM D 3174 standards, respectively. The fixed carbon was calculated using Equation 1:

Fixed carbon = 100 – (% moisture content + % ash content + % volatile matter). 1

The elemental analysis of corncob was carried out using CHNS Analyzer. The sulphur content of the sample was determined using a spectrophotometer and the amount of oxygen in the sample was obtained by adding the percentage total of carbon, nitrogen, sulphur and hydrogen and subtracting from 100 according to equation 2:

% Oxygen = 100 – (C + N + S + H) % 2

The higher heating value (HHV) of the sample was determined according to the ASTM D 240 standard test method using a bomb calorimeter (calorimetry equipment).

Design of Experiment using Response Surface Methodology (RSM)

D – Optimal Design of the Response Surface Methodology (RSM) was employed for the design of experiments for the non-catalytic pyrolysis. Another design was done at the condition for maximum bio-oil yield from the non-catalytic pyrolysis experiments to determine the appropriate various biomass/catalyst ratios for the study using the Mixture methodology in Design Expert software (version 13.0.1). Table 1 shows the minimum and maximum values of experimental parameters for the non-catalytic pyrolysis.

Table 1: Minimum and maximum values of experimental parameters

	Min	Max
Temp (℃)	450	600
Time (min)	20	35

Experimental Setup and Procedure

Two sets of experiments were conducted differently. The first set of experiments was conducted using a corncob without catalyst while the second set was conducted with the addition of a catalyst to the corncob. The non-catalytic pyrolysis experimental design with the number of runs was determined according to Design-Expert version 13.0.1. For the first set of experiments (non-catalytic pyrolysis), eleven samples (100g each) were prepared according to the number of runs from the experimental design and labeled runs 1 to 11. Each sample was charged into the reactor in preparation for thermal decomposition of the sample based on the experimental design for a specific range of temperature and holding time. To account for convective heat loss, the reactor temperature was set at 50 ℃ above the targeted temperatures. The condensing unit was immersed in an ice bath and connected to the reactor to facilitate volatile condensation, the gas receiver was employed to collect non-condensable gases and condensable vapour trapped in the condenser. After the prescribed holding time, the process was terminated and the char was removed from the reactor and allowed to cool and then measured as well as the bio-oil and expressed as percentages of the mass of the initial sample according to equations 3, 4 and 5.

$$\%\, Bio-oil\ \ yield = \frac{Mass\ of\ the\ liquid\ obtained\ after\ pyrolysis}{mass\ of\ the\ dried\ raw\ biomass}\ x\ 100 \qquad 3$$

$$\%\, Char\ yield = \frac{Mass\ of\ the\ char\ obtained\ after\ pyrolysis}{mass\ of\ the\ dried\ raw\ biomass}\ x\ 100 \qquad 4$$

$$\%\, Gas\ yield = 100 - (\%\, Bio-oil\ yield + \%\, Char\ yield\ ) \qquad 5$$

This procedure was followed for all other samples at different residence times and pyrolysis temperatures based on the experimental design. Each run was repeated twice and the average value of the reading was calculated. The optimum temperature and holding time for the bio-oil yield were then noted. The second set of experiments (catalytic pyrolysis) was carried out with samples of different biomass/catalyst (Corncob/ZnO) weight ratios (b/c ratio) of 100/0, 97.5/2.5, 96.67/3.33, 95/5, 93.33/6.67, 92.5/7.5 and 90/10 according to mixture methodology design of Design Expert software (version 13.0.1).

The samples were thoroughly mixed and were fed into the crucible, one at a time in preparation for the pyrolysis process. The temperature (550 ℃) of the optimum bio-oil yield of the non-catalytic experiment was pre-set as the temperature for each of the seven runs of the catalytic pyrolysis and the furnace heated with the aid of an electric heating element to a temperature of 600 ℃ (50 ℃ higher than the optimum temperature) to compensate for the heat loss during the insertion of the crucible. When the furnace attained the pre-set temperature, it was opened and the crucible was inserted into it. The furnace was then covered and reset to the actual optimum temperature (550℃) and a residence time of 25 min. Pyrolysis vapour was condensed into liquid in the ice bath-cooled condenser while the non-condensable gases were collected in the gas receiver. After each run, the liquid and char yields were weighed and expressed as a percentage of the weight of the initial raw sample of the corncob while gas yield was attained as previously stated in equations 3, 4 and 5. The ultimate analysis and fuel properties of the bio-oils were then determined. Figure 1 shows the exploded view of the pyrolysis unit used for the experiments at Foundry Workshop, LAUTECH, Ogbomoso.

Bio-oil Characterization

The bio-oil was characterized using a CHNS Analyzer to obtain the elemental composition and quality of the bio-oil.

Ultimate Analysis

The elemental analysis of the bio-oils was carried out with the same equipment used for the feedstock. The sulphur content of the sample was determined using a spectrophotometer and the amount of oxygen in the sample was obtained by mass balance.

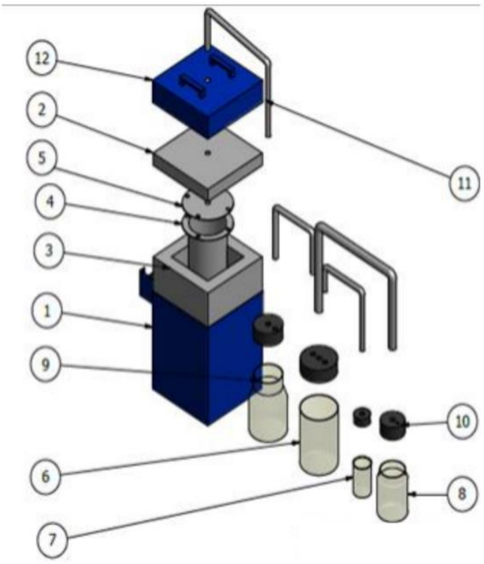
Fuel Characterization of Bio-oils

The fuel properties of the bio-oils were determined by standard methods. The pH value was determined using a calibrated Jenway ® 3520 pH meter. The kinematic viscosity of the bio-oils was determined by VV-III Ultra Programme Rheometer at 40℃ using the ASTM D445 standard method. Density was measured using a specific gravity bottle, also called a pycnometer. The flash point was determined according to the ASTM D93 standard test method. The cloud point was determined according to the ASTM D2500 standard. The pour point and ash content were determined according to ASTM D97 and ASTM D482-80 standards, respectively. The fire point was determined using a Pensky-Martens Open/Closed tester (heat exposure device) according to the ASTM D92 standard test method. Carbon Residue was determined using Conradson Carbon Residue (CCR) and Micro Carbon Residue (MCR) methods and the calorific value was determined according to the ASTM D240 standard test method for heat of combustion of liquid hydrocarbon fuels by Bomb calorimeter.

RESULTS AND DISCUSSION

Physicochemical Properties of Corn cob

The physicochemical properties of corncob are presented in Table 2. Proximate analysis showed the percentage of volatile matter (39.67 %) which increased the yields of liquid and gaseous fuel during pyrolysis (Lazzari et al., 2016). A higher proportion of volatile matter enhances the attractiveness of biomass as a feedstock for pyrolysis (Verma and Mondal,2017).



PARTS LIST		
ITEM	**QTY**	**PART NAME**
12	1	Casing cover
11	4	Pipe and Hose
10	4	Glass seal
9	1	Conical flask
8	1	Gas collection flask
7	1	Overflow flak
6	1	Flask 2
5	1	Crucible cover
4	1	Crucible
3	1	Furnace
2	1	Furnace cover
1	1	Metal casing

Figure 1: The exploded view of the pyrolysis unit

The proximate analysis of the corncob also showed the percentages of fixed carbon (33.29 %), moisture content (17.86 %) and ash content (9.19 %). A higher proportion of fixed carbon content enhances the calorific value of the sample. The HHV of the sample is 34.68 MJ/kg. Based on element composition, the feedstock (corncob) contained carbon (41.43 %), oxygen (32.73 %), hydrogen (16.88 %), nitrogen (8.86 %) and sulphur (0.09 %). This aligns with findings from the previously conducted studies (Lazzari *et al*., 2016).

Table 2 Physicochemical properties of Corn cob

Analysis	Component	Composition
Proximate (%)	Moisture content	17.86
	Ash content	9.19
	Fixed carbon	33.29
	Volatile matter	39.67
Calorific value (MJ/kg)		34.68
Ultimate (%)	Carbon	41.43
	Oxygen	32.73
	Hydrogen	16.88
	Nitrogen	8.86
	Sulphur	0.09
Atomic ratio (-)	H/C	4.89
	O/C	0.59
	N/C	0.18

The percentage of oxygen was 32.73 %, which is lower than the value reported for jute-stick (41.37 %) and bagasse (38.94 %) by Hassan *et al*. (2011) and pine wood (42.2 %) by Okekunle *et al*. (2012). A higher percentage of carbon with a low value of oxygen in the corncob sample makes it a good material for the production of biofuel. This is so because carbon aids the heating value of fuel while oxygen reduces it. The percentage of sulphur (0.09 %) and nitrogen (8.86 %) are low, indicating that the formation of sulphur (IV) oxide is at lower risk (Tsai *et al*., 2018) and the corncob is environmentally friendly as an energy source. This brings to bear the vital elements that influence energy value and emission.

Products Yields

Tables 3 and 4 show the results of the non-catalytic and catalytic pyrolysis of the corncob, respectively. The product yields (bio-oil, bio-gas and bio-char) from the pyrolysis experiments at different temperatures (450, 500, 550 and 600 °C) for non-catalytic and the optimum temperature, 550 °C and time 25 min for the catalytic results with different corncob/ZnO ratios are shown respectively. Figure 2 and 3 show the pictures of some bio-oils and bio-char yields collected during the experiment. From Table 3, the yields of bio-oil, bio-char and bio-gas for the non-catalytic experiments are in the range 33.44 - 44.94, 25.63 - 35.37 and 26.33 - 37.35 wt.%, respectively.

Table 3 Results of the non-catalytic pyrolysis of corncob

Run	Temperature (°C)	Time (min)	Bio-oil (%)	Bio-char (%)	Bio-gas (%)
1	450	20	35.30	35.37	29.33
2	450	25	37.80	29.82	32.38
3	450	30	39.51	34.16	26.33
4	450	35	44.93	28.48	26.59
5	500	25	35.14	30.46	34.40
6	550	20	33.44	29.21	37.35
7	550	25	44.94	27.31	27.75
8	550	35	38.46	25.63	35.91
9	600	20	35.84	29.02	35.14
10	600	25	37.54	31.25	31.21
11	600	30	39.56	30.28	30.16

Table 4 Results of the catalytic pyrolysis of corncob

Run	Temperature (°C)	Time (min)	Biomass (g)	Catalyst (g)	Bio-oil (%)	Bio-char (%)	Bio-gas (%)
1	550	25	100	0	27.70	27.12	45.18
2	550	25	97.5	2.5	27.91	27.47	44..62
3	550	25	96.67	3.33	30.10	34.45	35.45
4	550	25	95	5	30.71	32.48	36.81
5	550	25	93.33	6.67	34.54	33.01	32.45
6	550	25	92.5	7.5	33.57	33.99	32.44
7	550	25	90	10	37.45	36.46	26.09

The highest bio-oil yield (44.94 wt.%) was obtained at a temperature of 550 °C and a time of 25 minutes while the lowest bio-oil yield (33.44 wt.%) was also obtained at a temperature of 550 °C but at a time of 20 minutes. Table 4 shows the yields of bio-oil, char and gas from the catalytic pyrolysis at different biomass/catalyst ratios.

Results showed that the highest yields of bio-oil (37.45 %), char (36.46 %) and gas (45.18 %) were obtained at 90/10, 90/10 and 100/0 b/c ratio, respectively, while the lowest yields of bio-oil (27.70 %), char (27.12 %) and gas (26.09 %) were respectively obtained at 100/0, 100/0 and 90/10 b/c ratios at the optimum temperature of 550 °C and time of 25 minutes. That is, bio-oil has the highest yield at the corncob/ZnO blend ratio of 90/10 and the lowest yield at the corncob/ZnO blend ratio of 100/0. The bio-oil yields of the non-catalytic pyrolysis at all the different temperatures (450, 550 and 600 °C) except 500 °C were higher than the bio-oil yields of the catalytic pyrolysis experiments for all the blend ratios considered. This may be due to the more refined bio-oil obtained from the catalytic pyrolysis experiment. Figures 4, 5 and 6 show the combined effects of temperature and time on the bio-oil, bio-char and bio-gas yields of non-catalytic pyrolysis experiments respectively. It can be observed that initially, the bio-oil yields of 35.30 wt.% increased from 450 °C at the time of 20 minutes to 38.46 wt.% at 550 °C and time of 35 minutes and decreases thereafter to 35.84 wt.% with further increase in temperature at 600 °C and time of 20 minutes which shows that increased in the temperature and time increased the yield of bio-oil. It can be seen that, at 450 °C, 20 minutes, the bio-char is very high and as time was increasing to 35 minutes, bio-char was dropping. Also, the biochar yield decreased from 35.37 % to 30.28 % as the temperature increased from 450 °C to 600 °C at the times of 20 minutes and 30 minutes respectively.

The biochar yield agreed with the pyrolysis convention that an increase in pyrolysis temperature decreases char yields (Okekunle *et al.*, 2021).

Figure 2: Bio-oils obtained during the pyrolysis experiment

Results also showed that bio-gas yield increased with increasing temperature, 32.38 % at 450 °C and time of 25 minutes to 34.40 % at 500 °C and time of 25 minutes, to 37.35 % at 550 °C and time of 20 minutes, which shows that as the temperature and time were increasing and decreasing respectively, biogas was increasing. This finding is in agreement with a few other studies where lower biochar yields and higher gas yields were observed for increasing temperature (Asadullah *et al.*, 2007; Sensoz *et al.*, 2006).

Figure 3: Bio-char obtained during the pyrolysis experiment

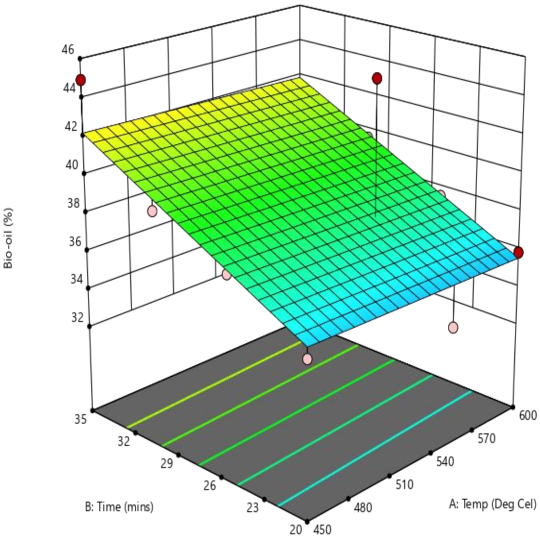


Figure 4: Combined effects of temperature and time on non-catalytic pyrolysis bio-oil yield.

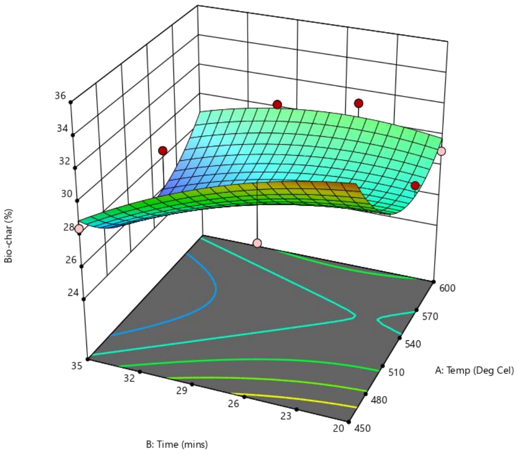


Figure 5: Combined effects of temperature and time on non-catalytic pyrolysis bio-char yield

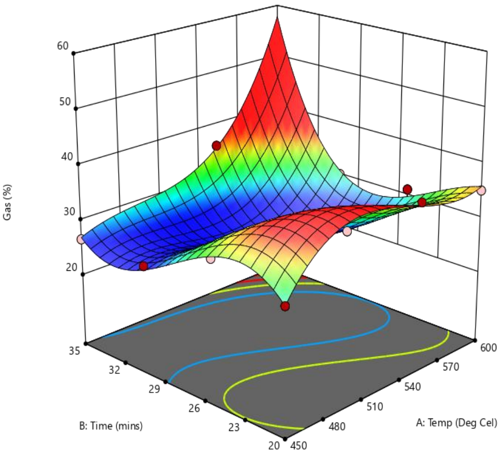


Figure 6: Combined effects of temperature and time on non-catalytic pyrolysis biogas yield

Table 5 Elemental composition and HHVs of bio-oils obtained at optimum temperature and biomass/catalyst ratios

T (^{0}c)	B/C ratio (-)	Element (wt.%)					Atomic ratio (-)			HHV (MJ/kg)
		C	H	N	S	O	H/C	O/C	N/C	
550	100/0	47.08	19.18	8.40	0.07	25.28	4.88	0.40	0.153	26.22
550	97.5/2.5	45.75	18.64	7.18	0.08	28.35	4.89	0.46	0.134	25.16
550	96.67/3.33	49.28	20.08	6.68	0.07	23.90	4.89	0.36	0.116	25.04
550	95/5	44.21	18.01	7.17	0.08	30.53	4.88	0.51	0.139	24.77
550	93.33/6.67	44.13	17.98	7.17	0.08	30.65	4.89	0.52	0.139	25.11
550	92.5/7.5	49.61	20..21	6.41	0.07	23.70	4.88	0.35	0.111	26.19
550	90/10	45.01	18.34	6.47	0.06	30.13	4.89	0.50	0.123	25.32

Elemental Analysis of Bio-oils

Table 5 shows the results of the elemental analysis, atomic ratio and HHV of the bio-oils from catalytic pyrolysis experiments obtained at the optimum conditions (550 °C) and time (25 minutes) at various biomass/catalyst ratios. As shown in the table, the bio-oils derived from catalytic pyrolysis are richer in carbon (49.61 %) at a b/c ratio of 92.5/7.5 and 49.28 % at a b/c ratio of 96.67/3.33 than that obtained from non-catalytic pyrolysis (47.8 %).

The bio-oils from catalytic pyrolysis are also richer in hydrogen (20.21 %) at b/c ratio of 92.5/7.5 and 20.08 % at b/c ratio of 96.67/3.33 than that obtained from non-catalytic pyrolysis (19.18), but lower in oxygen (23.70 %) at b/c ratio of 92.5/7.5 and 23.90 % at b/c ratio of 96.67/3.33 than that obtained from non-catalytic pyrolysis (25.28 %) at the same temperature and time. These results are in agreement with the findings of Zhou *et al*. (2013), who reported higher percentages of carbon (49.73 wt.%) and hydrogen (12.57wt.%) with a lower oxygen percentage (35.62 wt.%) for bio-oil from catalytic pyrolysis than the values obtained for non-catalytic pyrolysis bio-oil, with carbon (49.20 wt.%), hydrogen (11.65 wt.%) and oxygen (36.78 wt.%). It is expected that for high-quality fuel, carbon and hydrogen contents should be high and oxygen content should be low, as these values influence the calorific value of fuels.

These results also showed that catalysts help in deoxygenating bio-oils (Putun, 2010). Oxygen reduction in catalytic pyrolysis bio-oils will improve their stability and enhance their upgrading to hydrocarbons (Shah *et al*., 2012) because oxygen in bio-oil has been identified as a source of bio-oil instability (Bardalai and Mahanta, 2015). Upgrading bio-oil to hydrocarbons also requires oxygen removal (Shah *et al*., 2012).

The presence of ZnO catalyst reduced the percentage of sulphur in catalytic pyrolysis bio-oils (0.06 %) at a b/c ratio of 90/10, compared to the value for bio-oil from non-catalytic pyrolysis (0.07 %). This implies that SOx emissions from the combustion of catalytic pyrolysis bio-oils will be lower than those from non-catalytic pyrolysis bio-oil, which makes bio-oils from catalytic pyrolysis more environmentally friendly. The H/C ratio for bio-oils from catalytic pyrolysis of 4.89 at a b/c ratio of 90/10, 93.33/6.67, 96.67/3.33 and 97.5/2.5 are identical to that of non-catalytic pyrolysis with 4.89. An identical H/C ratio indicates that both catalytic and non-catalytic pyrolysis bio-oils have a similar balance between hydrogen and carbon atoms or it may be due to possible catalyst deactivation which could lead to similar product distributions (Zhang *et al*., 2010).

The observation of identical H/C ratio in catalytic and non-catalytic bio-oils also indicates that the catalyst (ZnO) used affected aspects of the catalytic bio-oils composition such as stability and de-oxygenation without changing the fundamental H/C balance (Ebrahim and Amani, 2015). O/C ratios for catalytic pyrolysis bio-oils, 0.35 and 0.36 at b/c ratios of 92.5/7.5 and 96.67/3.33 are lower than that obtained for non-catalytic pyrolysis bio-oil (0.40). These results are in agreement with the findings of Putun (2010) and Zhou *et al*. (2013) who reported lower O/C ratios for bio-oils from catalytic pyrolysis compared to the values obtained from non-catalytic pyrolysis. The Higher Heating Values (HHVs) of the catalytic pyrolysis bio-oils are lower than those of the non-catalytic pyrolysis bio-oil. Oxygen and carbon contents of catalytic pyrolysis bio-oils at b/c ratio of 97.5/2.5, 95/5, 93.33/6.67, and 90/10 were higher and lower during catalytic reactions respectively which contributed to the lower heating values compared to the non-catalytic pyrolysis bio-oil.

Basic Fuel Properties of Bio-oil

The basic fuel properties of the bio-oils from catalytic pyrolysis at the optimum temperature with different corncob/ZnO blend ratios were compared with that of the bio-oil from non-catalytic pyrolysis at the same temperature. The maximum bio-oil yield (37.45wt.%) from catalytic pyrolysis at optimum temperature (550 °C) was obtained at a biomass/catalyst ratio of 90/10.

Viscosity

Figure 7 shows the viscosity of the bio-oils from catalytic pyrolysis compared with that of non-catalytic pyrolysis at the optimum temperature of 550 °C. The viscosity of the catalytic pyrolysis bio-oils varied from 0.276 – 0.476 mm^2/s and that of non-catalytic pyrolysis bio-oil is 0.515 mm^2/s.

As shown in the figure, the presence of a catalyst reduced the viscosity of bio-oils at all b/c ratios and for non-catalytic pyrolysis bio-oil, the viscosity is high (Shadangi and Mohanty, 2014). Viscosity will affect fluid flow if it is too high, then flow-ability is hindered and can bring about intermittent combustion in the sense that the fluid will not flow as it should. High viscosity poses a challenge during atomization in the use of bio-oil as fuel in diesel engines (Shadangi and Mohanty, 2014).

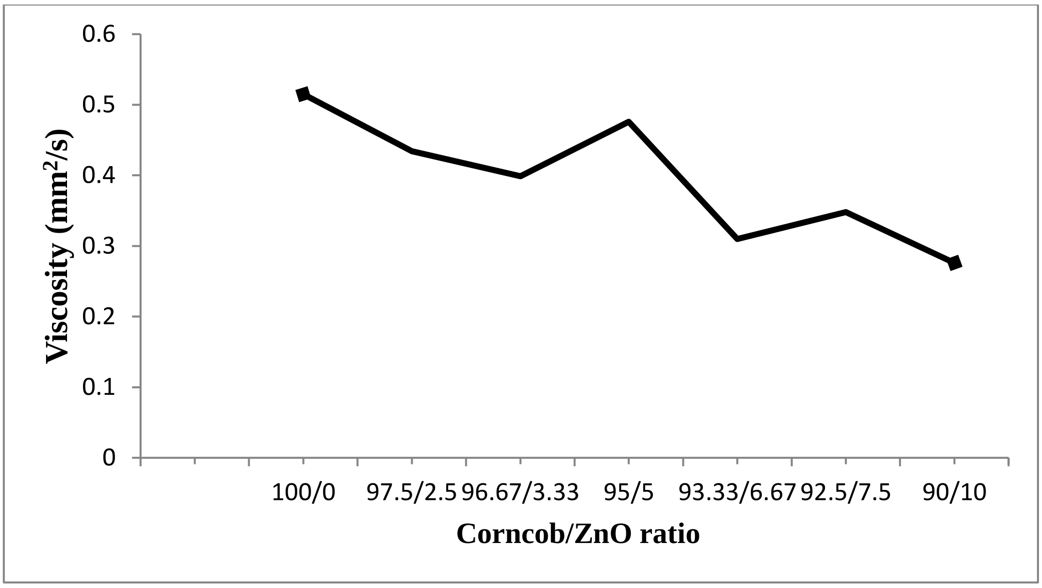


Figure 7: Viscosity of the bio-oil at various biomass/catalyst ratio

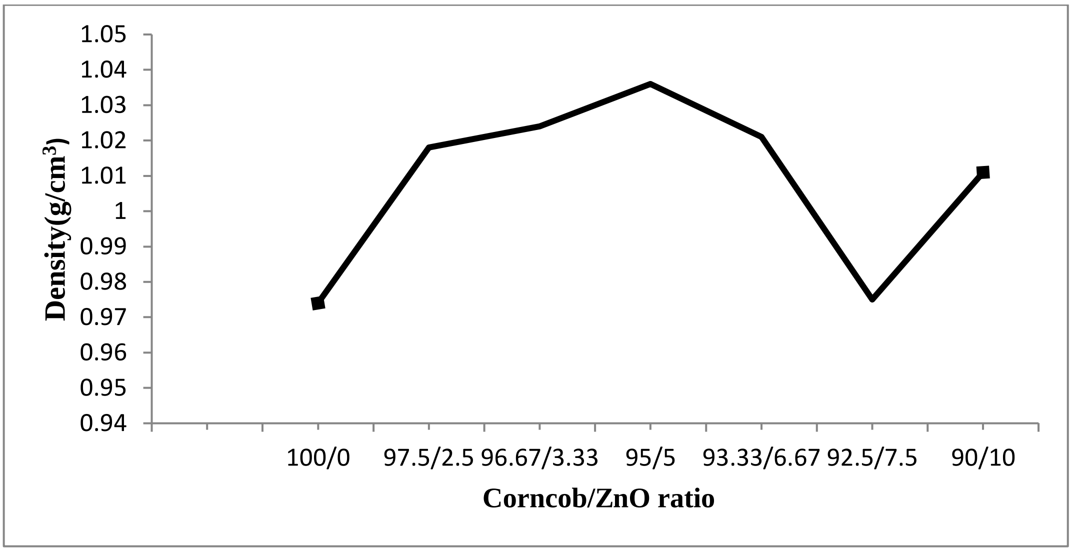


Figure 8: Density of the bio-oil at various biomass/catalyst ratios

Low viscosity is preferable in combustion processes to ensure efficient fuel flow and engine compatibility (Luo *et al*., (2011); Baldos *et al*., (2013). The viscosities of the catalytic pyrolysis bio-oils obtained in this study are much lower than the 2.85 mm^2/s reported by Guptal *et al*., (2019). These results showed that catalytic pyrolysis bio-oils have a lower tendency of internal resistance to free motion and therefore less restricting tendency to flow than non-catalytic pyrolysis bio-oils thus becoming a better fuel in winter and other colder environments.

Density

Figure 8 shows the comparison between the density of catalytic pyrolysis bio-oils and non-catalytic bio-oils. The density of catalytic pyrolysis bio-oil obtained at the optimum temperature varied within the range of 0.975 – 1.036 g/cm^3 compared to the non-catalytic pyrolysis bio-oil with 0.974 g/cm^3. Almost similar values were reported by Gupta *et al*., (2021), Ahmed *et al*., (2018) and Gupta *et al*., (2019). The density of catalytic pyrolysis bio-oils obtained in this study is higher than that of non-catalytic pyrolysis bio-oil because there are still many impurities in the bio-oil and are heavier than that of high-speed diesel of density 0.840 g/cm^3. The high density of bio-oil is directly related to heavy fractions and energy contents (Sensoz *et al.*, 2006). Low-density bio-oil tends to offer a better balance for combustion applications, providing sufficient energy density while maintaining favourable handling and combustion characteristics (Bridgewater, 2012). Abdullahi and Gerhauser (2008) described bio-oil as a highly dense liquid with a density of around 1.20 g/cm^3, which is higher than the values of density obtained for the bio-oils in this study.

pH value

The pH values of the bio-oils from the catalytic pyrolysis at optimum temperature varied from 5.48 to 5.66 compared with that of the bio-oil from non-catalyst pyrolysis of the same temperature, which is 5.60 as shown in Figure 9. The catalytic pyrolysis bio-oil has the highest value of pH (5.66) at the biomass/catalyst ratio of 90/10, higher than the pH value of the non-catalytic pyrolysis bio-oil with 5.60. As shown in the Figure, ZnO catalyst increased the pH value of the bio-oils at a b/c blend ratio of 95/5 and 90/10. These results are in agreement with the findings of Shadangi and Mohanty (2014), who reported an increase in pH values of the bio-oils from catalytic pyrolysis of Niger seed as compared to those of bio-oils from non-catalytic pyrolysis of the same biomass material. However, at b/c blend ratio of 97.25/2.5, 96.67/3.33 and 92.5/7.5, the pH values of the bio-oil from catalytic pyrolysis were lower than that of the bio-oil from non-catalytic pyrolysis. This may be linked to the difference in the b/c ratio that gave the optimum yield of bio-oil at 550 ℃. Lower pH values make bio-oils acidic, which can cause damage to internal combustion engines when bio-oils are used.

The pH values of all catalytic pyrolysis bio-oils in this study are higher than the values (2.7 to 3.3) reported by Okekunle *et al.*, (2021) and the values (2.0-3.8) reported by Garcia *et al.*, (2002) and 3.3 obtained in literature for Jatropha seed coat (Manurung *et al*, 2009). Higher pH values (as the value approaches 7, being neutral) are desirable for bio-oils since acidity can wear out the engine components when the bio-oil is used as fuel.

Ash Content

Figure 10 shows the comparison of ash content in the bio-oils obtained from the catalytic and non-catalytic pyrolysis process at the optimum temperature (550 ℃) of the bio-oil. The ash content in the bio-oils has its highest value (0.022 %) at b/c blend ratio of 90/10 and its lowest value (0.011 %) at b/c blend ratio of 97.5/2.5 and is lower compared to the value of ash content in the non-catalytic pyrolysis bio oil (0.014 %) and lower compared to 0.7 % reported by Oyebanji *et al.* (2017).

High ash content is not desirable as it brings down the energy value of the fuel. Low ash content is desirable in pyrolysis bio-oil for combustion applications. It suggests a cleaner bio-oil with fewer organic impurities which enhances its suitability for combustion processes. Ash content at b/c ratios of 95/5, 93.33/6.67, 92.5/7.5 and 90/10 were higher than that of non-catalytic pyrolysis bio-oil. This may be due to operational conditions like fluctuations in residence time in accelerating catalyst degradation and ash deposition or catalyst components may leach into the bio-oil contributing additional ash-forming materials during pyrolysis (Scarlat and Sharma, 2015) The ash contents of both catalytic (0.011-0.022 %) and non-catalytic pyrolysis bio-oils (0.014 %) are lower than the range (0.03-0.3 %) reported by Yu *et al.* (2007).

Carbon residue

Figure 11 shows the carbon residue of the bio-oils from catalytic and non-catalytic pyrolysis at the optimum temperature. Carbon residue is a measure of the coke-forming tendencies of fuel oils.

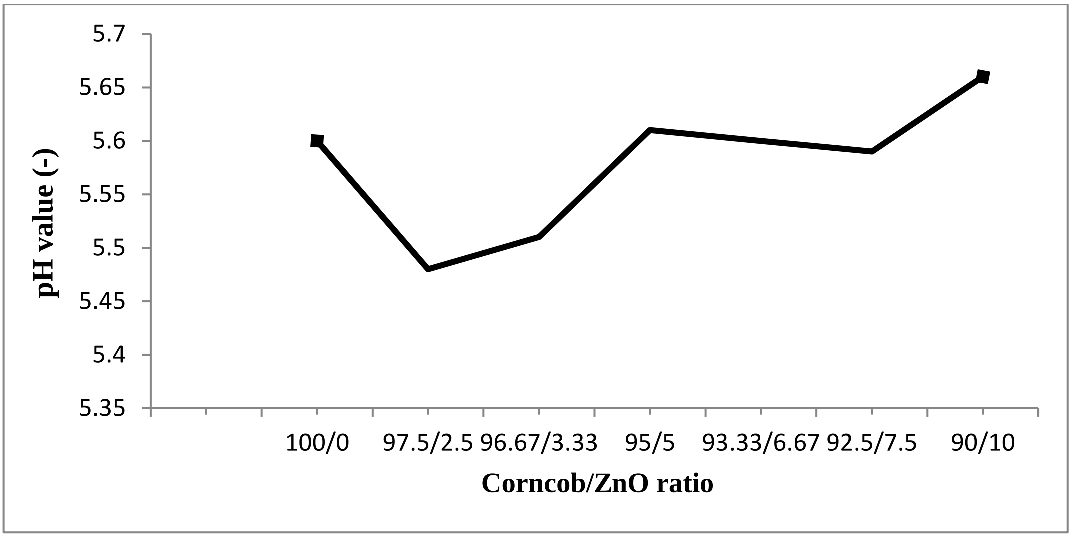


Figure 9: pH value of the bio-oil at various biomass/catalyst ratios

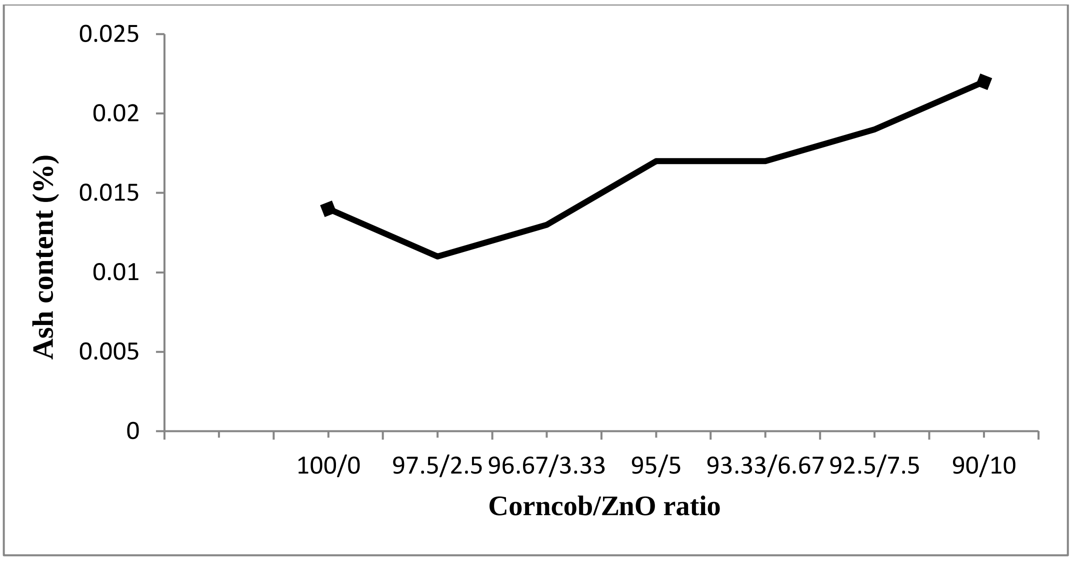


Figure 10: Ash content of the bio-oil at various biomass/catalyst ratios

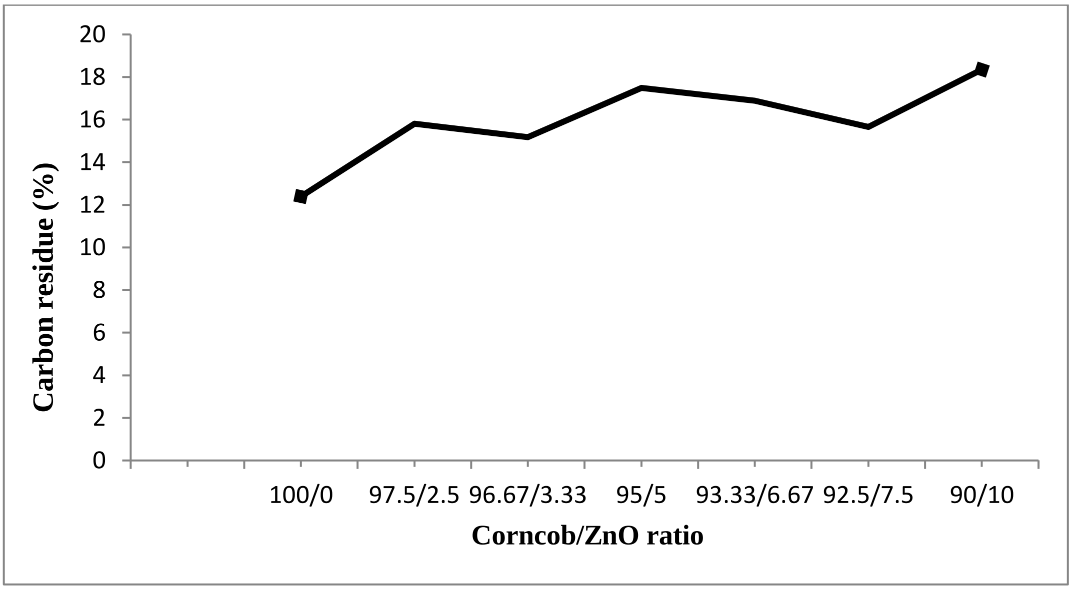


Figure 11: Carbon residue of the bio-oil at various biomass/catalyst ratios

The figure shows that the carbon residues for the catalytic pyrolysis bio-oils (15.18-18.35 %) are higher than the values obtained for non-catalytic pyrolysis bio-oils (12.39 %). Higher carbon residue in these bio-oils can result from lower oxygen content with the presence of a catalyst which enhanced de-oxygenation while producing more aromatic coke-prone compounds compared with non-catalytic pyrolysis bio-oil that produces bio-oil with higher oxygenated compounds and results in lower carbon residue. The carbon residue values of the bio-oils can be reduced further with the use of polar solvents in extracting complex polar heavy structures (Anouti *et al*., 2016). The values of carbon residue for both catalytic and non-catalytic bio-oils are lower than the values (18-23 wt.%) reported by Garcia-Perez *et al*. (2002) except at b/c ratio of 90/10 with 18.35 wt.%.

Pour point

Figure 12 shows the pour point of catalytic pyrolysis bio-oils compared with that of the non-catalytic pyrolysis bio-oil. The pour point of the non-catalytic pyrolysis bio-oil (12.8 ℃) is higher than that of the catalytic pyrolysis bio-oil (10.3-12.5 ℃) which shows that the use of a catalyst reduced the pour point of the catalytic pyrolysis bio-oils. The pour point of a bio-oil is evidence of the minimum temperature at which the bio-oil can flow (Oasmaa and Peacock, 2010) and is very useful for the evaluation of the quality of the fuel and depends mainly on the chemical structure and the composition of the bio-oil which also determines the fuel fluidity at low temperatures. The pour point of the catalytic pyrolysis bio-oils in this study are higher than those reported by Weerachanchai *et al*. (2007) (-17 to 1℃), Okekunle *et al*. (2021) (-25 to –28 ^{0}C) and Thomas (2018) (-36 to 9 ℃). Since pour point is the minimum temperature at which bio-oil can flow, the bio-oils obtained in this study would require as low as 10.3 ℃ before it could start losing its ability to flow and may be suitable for use in moderate to warm countries (temperate climates) and will require treatment before use in extremely cold countries.

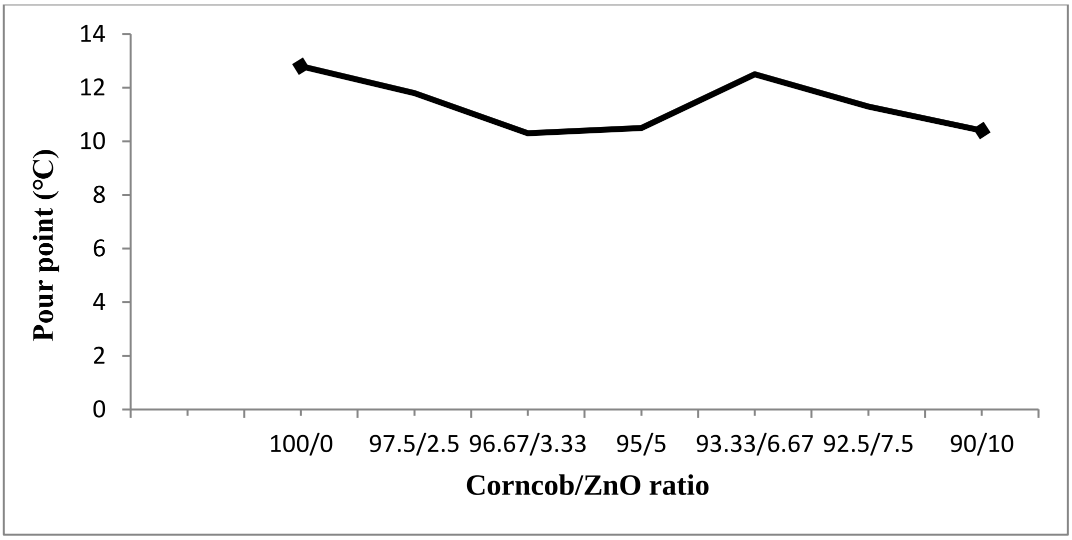


Figure 12: Pour point of the bio-oil at various biomass/catalyst ratios

Cloud point

The cloud points of catalytic pyrolysis bio-oils and non-catalytic pyrolysis bio-oils are shown in Figure 13. As shown in the figure, the cloud points of all the catalytic pyrolysis bio-oils (16.4-18.2 ℃) are lower than that of non-catalytic pyrolysis bio-oil (18.3 ℃) except at the b/c ratio of 95/5 (19.2 ℃). The cloud point is the highest temperature at which a cloud of waxy crystals becomes visible or the temperature at which bio-oil becomes cloudy or hazy, and the presence of this crystal can hinder fuel flow in combustion processes and for the fuel line not to being blocked, the temperature in running the engine must always be higher than the cloud point, otherwise, it will impair the flow of fuel and can cause clogging. Cloud points should be as low as possible for optimal engine performance and compatibility. The use of a catalyst reduced the cloud point of bio-oil at b/c ratios of 97.5/2.5, 96.67/3.33, 93.33/6.67, 92.5/7.5 and 90/10, and it would be better to operate the reactor or the pyrolysis experiment at those b/c ratios to have the cloud point as low as possible. At a b/c ratio of 95/5, the cloud point is high and may be attributed to the molecular weights of the components in the bio-oil (Hossain *et al.*, 2019).

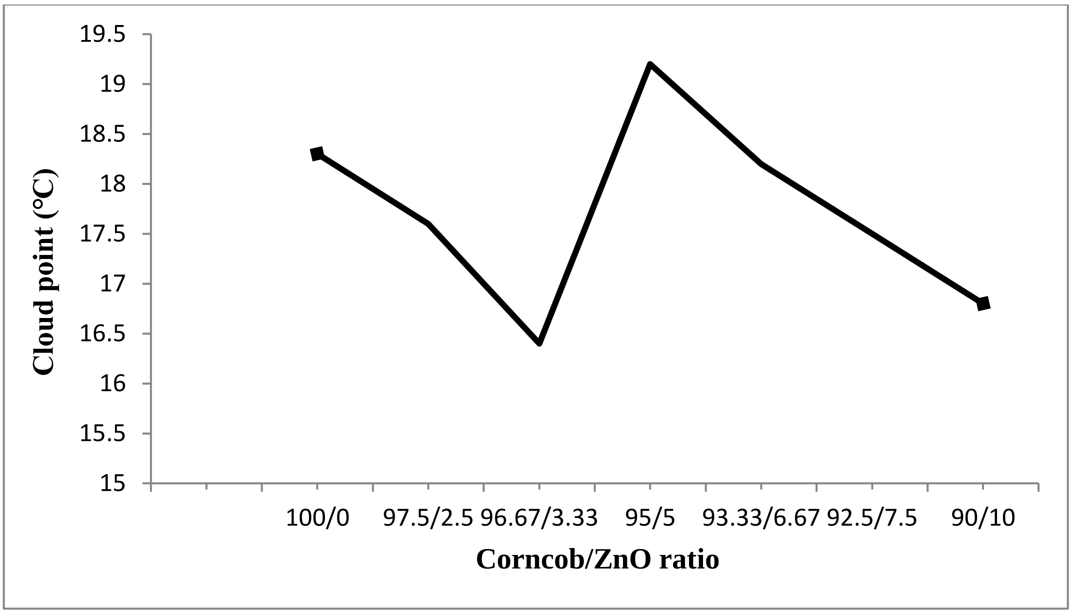


Figure 13: Cloud point of the bio-oil at various biomass/catalyst ratios

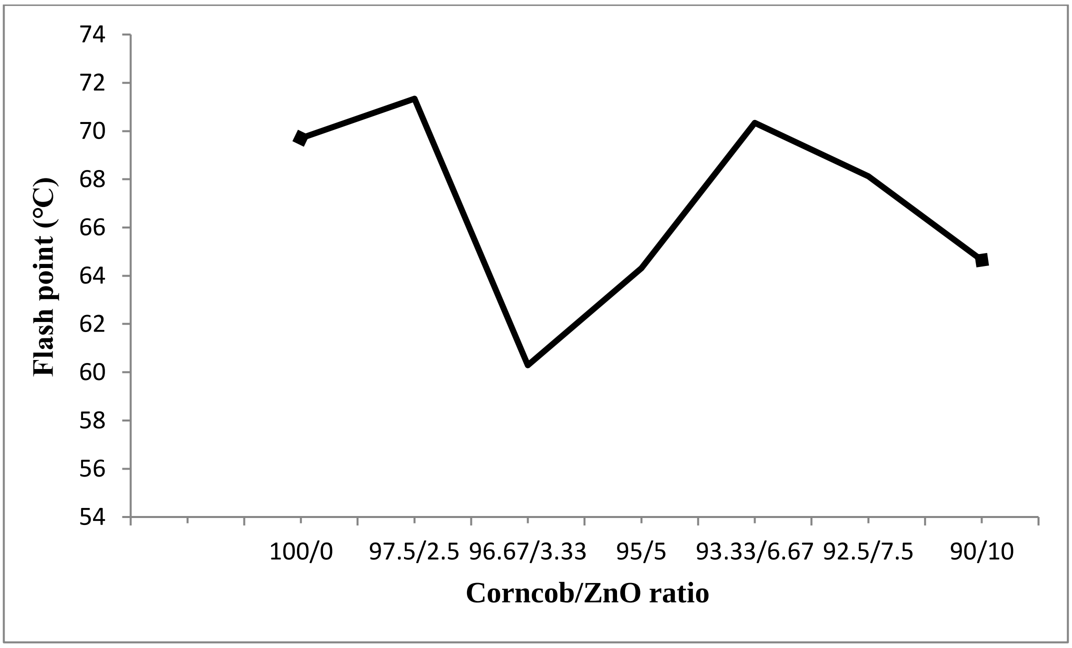


Figure 14: Flash point of the bio-oil at various biomass/catalyst ratios

Flash point

Figure 14 shows the comparison of the flash point of the bio-oils obtained from catalytic pyrolysis with that of a non-catalytic experiment. As shown in the figure, at b/c ratios of 97.5/2.5 and 93.33/6.67, the bio-oil cloud points were 71.34 and 70.34 ℃, respectively which are higher than the flash point of the non-catalytic pyrolysis bio-oil (69.7 ℃). In terms of volatility, the flash point of bio-oils has an impact on their use as fuel (Idris *et al*., 2020). A higher flash point signifies the bio-oil is safer to handle and lowers the risk of accidents that might occur from vapour ignition, that is, fuel with a higher flash point is less flammable or hazardous, making the oils safer to handle and transport. The results therefore, showed that the catalytic pyrolysis bio-oils at 97.5/2.5 and 93.33/6.67 b/c ratios obtained in this study are safer in terms of handling and storage and are less hazardous. The flash point of both the catalytic pyrolysis bio-oils and the non-catalytic pyrolysis bio-oil in this study (60.29 – 71.34 ℃) is higher than that of petroleum diesel (58.5 ℃) (Khan et al., 2016).

Fire Point

Figure 15 shows the fire points of the bio-oils obtained from both the catalytic at different b/c ratios and non-catalytic pyrolysis experiments at the optimum temperature (550 ℃). As shown in the figure, the fire points of the bio-oils obtained from catalytic pyrolysis (73.5-77.4 ℃) are higher than that of non-catalytic pyrolysis (72.2 ℃) except the fire point at the b/c blend ratio of 96.67/3.33 with 71.2 ℃. The fire point is the temperature at which vapours from the oil ignite and continue to burn when exposed to an open flame. A high fire point is desirable in pyrolysis bio-oil because it affects the safety, performance and combustion characteristics of the bio-oil. This implies that the catalytic pyrolysis bio-oils obtained in this study are preferable in terms of safety, storage stability and compatibility with combustion engines. The fire points of the catalytic and non-catalytic pyrolysis bio-oils in this study are also in the range of diesel flash point range (62-106 ℃) (Pandey and Kumar, 2020).

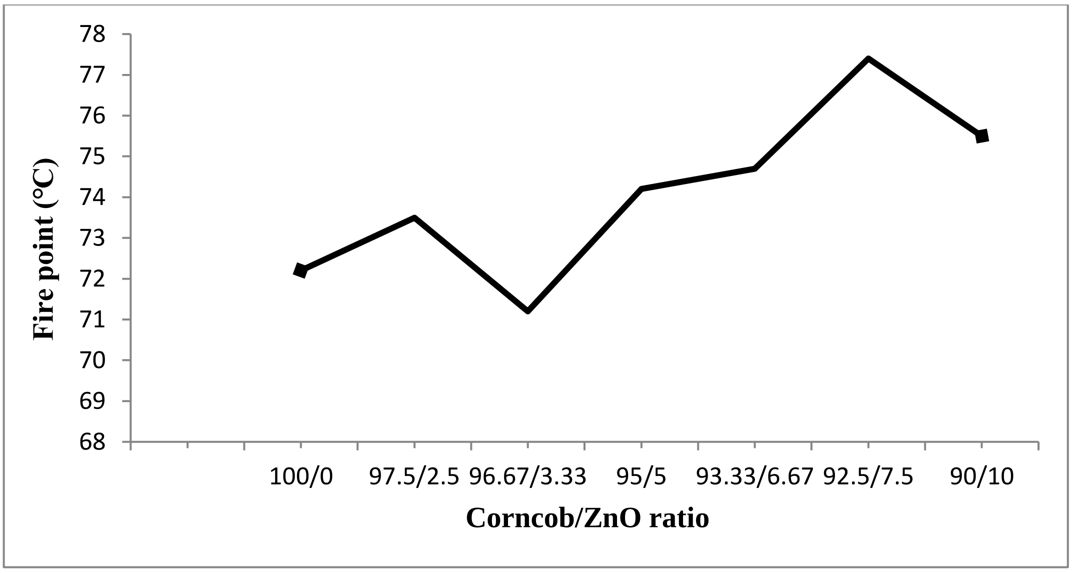


Figure 15: Fire point of the bio-oil at various biomass/catalyst ratios

Higher Heating Value (HHV)

Figure 16 shows the higher heating values of the bio-oil obtained from both non-catalytic and catalytic pyrolysis experiments. The HHVs of the catalytic pyrolysis bio-oil are in the range 24.77 – 26.19 MJ/kg and that of the non-catalytic pyrolysis bio-oils is 26.22 MJ/kg. The HHV is indicative of the hydrogen-to-carbon ratio. The HHVs of the catalytic pyrolysis bio-oils are lower than that of the non-catalytic pyrolysis bio-oil. This may be attributed to diverse factors such as increased oxygenation, water formation, altered molecular composition and operational conditions (Demirbas, 2004). Oxygen is detrimental to the heating value of fuels and was discovered that the oxygen content for non-catalytic pyrolysis bio-oil is low and therefore has higher heating value. Oxygen and carbon contents of catalytic pyrolysis bio-oils at b/c ratios of 97.5/2.5, 95/5, 93.33/6.67, and 90/10 were higher and lower during catalytic reactions respectively which contributed to the lower heating values compared to the non-catalytic pyrolysis bio-oil. The catalyst may be affecting other aspects of the catalytic bio-oil's chemistry such as increasing oxygenated functional groups or altering molecular structure in a way that reduces their HHV. The HHV of non-catalytic and catalytic pyrolysis bio-oils obtained in this study are lower than those of conventional gasoline (44-46 MJ/kg) and diesel (43.06 MJ/kg) specifications. According to Khuenkaeo and Tippayawong (2020), the HHV of bio-oils derived from pyrolysis of coconut shell and bamboo were 25.3 and 20.4 MJ/kg, respectively which are all lower than the calorific values of the catalytic and non-catalytic pyrolysis bio-oils in this study. The high energy value reflects the ratio of carbon to oxygen in the bio-oil.

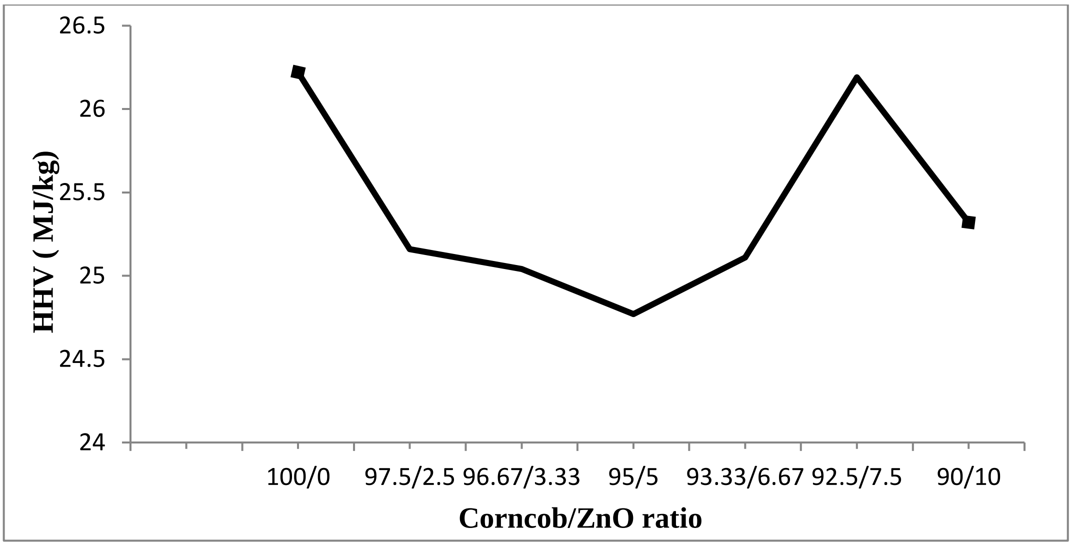


Figure 16: HHV of the bio-oil at various biomass/catalyst ratios

CONCLUSIONS

The effect of Zinc Oxide on the quality of the bio-oil from pyrolysis of *Zea mays indentata* corncob at different biomass/catalyst ratios at optimum temperature and time has been investigated, analysed and compared with that of non-catalytic pyrolysis bio-oil. The feedstock analysis revealed that corncob has a high potential for bio-fuel production because of its high carbon and hydrogen content with low sulphur content. The optimum condition for bio-oil yield (44.9 %) from thermal pyrolysis of corncob was obtained at the temperature of 550 ℃ and a time of 25 minutes. The optimum biomass/catalyst ratio for bio-oil yield (37.45 %) at the optimum process conditions of 550 ℃ and 25 minutes was at b/c of 90/10. Elemental analysis showed that catalytic pyrolysis bio-oils are richer in carbon and hydrogen at b/c ratios of 96.67/3.33 and 92.5/7.5, respectively but leaner in sulphur and oxygen at b/c ratios of 90/10, and 96.67/3.33 and 92.5/7.5, respectively than non-catalytic bio-oil. The use of ZnO as a catalyst in pyrolysis improved the fuel properties of bio-oils by reducing their kinematic viscosity at all b/c ratios, ash content at b/c ratios of 97.5/2.5 and 96.67/3.33, and increasing the pH values at b/c ratios of 90/10 and 95/5, compared with non-catalytic pyrolysis bio-oil. The results showed that catalytic pyrolysis bio-oils are safer in handling and storage and less hazardous. Based on the findings of this research, corncob has a high potential for biofuel production and could be exploited as an alternative source of fuel. The catalytic effect can be observed with different biomass-catalyst ratios in the future.

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