Comparative Study Of Non-Catalytic And Catalytic Pyrolysis Of Biomass To Produce Bio-Oil And Comparison Of The Bio Oil With Crude Oil

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***Abstract*—The pyrolysis of cassava peels (Manihot esculenta) and catholic vegetable (Jatropha tanjorensis) have been carried out with and without catalyst at temperatures of 459oC, 550oC and 700oC and particles of 300um, 399-600µm and 1000-1700µm. The catalysts used were ash from natural waste material such as cow bone ash and aroma fish scale ash. From the non-catalytic pyrolysis, it was observed that the bio oil yield from catholic vegetable was higher than the yield from cassava peels at all temperatures and particle size fractions 300µm, 300-600µm and 1000-1700µm investigated. The catalytic pyrolysis was carried with catalyst to biomass ratio of 1:15g, 2:15g and 3:15g.using catholic vegetable of 300µm. The bio oil produced with cow bone ash was higher than the oil produced using the arowana fish scale ash for all temperatures. The analysis of the physiochemical properties of the oils produced from the non-catalytic of catholic vegetable and cassava peels gave dark brown color for both oils, pH of 4.4 and 3.7, viscosity of 0.753cSt and 0.827cSt, Density of 0.823 and 0.816, API gravity of 40.05 and 42.0, acidity of 12.50mgKOH/g and 480mgKOH/g respectively. The results were compared to light crude oil and most of the properties were similar to those of crude oil. However, the acidity of the bio oils was significantly higher than that of light crude oil.**

Keywords—biomass, bio oil, catalytic pyrolysis, non- catalytic pyrolysis, crude oil,

I. INTRODUCTION

The motivating interest in utilizing biomass residues in the energy sector which are dumped as waste is as result of the fact it serves as sustainable energy sources. This waste-to-energy approach is more advantageous to the economy than waste treatment which cost money. Biomass waste is one of the renewable energy options to produce bio oil and has received significant attentions as a renewable fuel [1, 2]. Over the years, crude oil has been used as an energy resource to meet global energy demand [3]. The refined products have been useful in the transportation sector, electricity generation as well as other uses. However, the utilisation of crude oil produces greenhouse gases (GHGs) which are known to cause global warming and other health hazards. The potential of bio-oil to substitute crude oil is still not established due to some of the properties that make it unsuitable for the use in the existing refineries [4] such as high viscosity and acidity [5]. However, the development of biomass in Nigeria as a clean source of fuel is promising because its utilization does not produce CO_2 emissions [6], their abundant availability [7], high energy content [8] and low cost [9]. Hence, biomass energy research is attracting interest as an alternative fuel to crude oil and other fossil fuels.

Cassava (manihot esculenta) is a staple food resource in Nigeria and it is extensively cultivated. Cassava is usually peeled before using the tuber for various purposes. It is used in different industries to produce adhesives, plastics, chemical and other useful products [10]. Most of the times, the cassava peels are dumped on certain areas or burnt thereby causing environmental and health hazards since they contain cyanogenic glucosides [10] which releases hydrogen cyanide. Therefore, the utilisation of cassava waste to produce oil will not only be of benefit to the energy and transportation sector but also to safeguard human life. Some of the agricultural waste pyrolysed are rice husk, straw, corn cob, rice straw, cassava peels, sugarcane baggase, palm kernel shell [11,12,13]. The yields of bio-oil during pyrolysis process have been found to depend on the pyrolysis temperature.

Catholic vegetable (Jatropha tanjorensis) popularly called 'Hospital Too Far' in Nigeria because of its properties and its potential to remedy malaria and enhance blood production in the human [14]. It is a shrub, 6m high with spreading branches and stubby twinges. The potential of this biomass to produce bio oil would be investigated because of it fast growth rate. It can grow anywhere and needs little or no human intervention to fully mature and therefore can be planted as purpose grown biomass for bio oil production with interfering with it medicinal uses.

In order to enhance bio oil production from biomass feed stocks, researchers have investigated the effect of catalysts on the yield of bio oil or some parameters in the bio oil through pyrolysis [15]. However, catalyst active site poisoning is a factor that limits the process. Secondly, changes may occur in the pore structure of the catalyst due to bio char or coke deposition and may reduce the catalytic activity [4,16]. Alper et al, [17] investigated biomass pyrolysis using and observed that the catalyst activity decreased after every pyrolysis process. Furthermore, the cost of catalysts and the process of catalysts recovery when using chemical catalysts will increase bio oil production. Therefore, the use of cheap and efficient waste materials as a catalyst in biomass pyrolysis will be of economic value to bio oil production process. Cow bone is being dumped as waste in most parts of Nigeria since it has not found usefulness in many industries. The arowana fish scale is usually removed from the fish and dumped as waste. Till date no researcher has found any usefulness of the fish scale ash as catalysts. In the other hand, characterization of bio-oil produced through pyrolysis has been investigated [18, 19, 20]. Physical properties such as appearance, pH, density, viscosity, acidity, and other parameters have been analyzed. Also, elemental composition of the bio-oil produced has been characterized including empirical formula [21]. Hence, these studies investigates the pyrolysis behavior of cassava peels and catholic vegetable, the effect of natural inexpensive catalysts on bio oil production and compare the properties of bio oil produced with crude oil properties in order to provide information for upgrading of bio oil to fit into existing refineries petroleum

2.0 Materials and Experimental Procedure

2.1 Biomass sample, preparation

The two biomass samples used were cassava peels and catholic vegetable. Fresh cassava peelings were collected from farmers after harvesting and sun dried for 2 days. The leaves of Catholic vegetable were collected and sun dried for 2 days. The two samples were pulverised and sieved into different sizes: <300µm, 300-600µm and 1000-1700µm. The properties of the samples were determined by proximate analysis

2.2 Proximate analysis

The proximate analysis of the samples was carried out using the standard method as described elsewhere [22].

2.2.1 Moisture content

3g of the feed (sieved) of particle size 1000 – 1700µm was weighed as Weights w1. The crucibles were placed in an oven heated at 105^{o}C until constant weight. The sample was transferred to a desiccator to cool and then re-weighed as weights w_2. The moisture content was calculated by the following formula.

2.2.2 Volatile Matter (VM)

The sample (w_2) was put into a muffle furnace but this time the crucible was covered with a lid. It was heated for 10 minutes at 850^{o}C. The crucible was then placed in a desiccator to cool and then re-weighed as weights w_3. The % volatile matter was calculated as the difference in the weights (weight 2-weight 3).

2.2.3 Ash Content (A)

The sample weight (w_3) in a crucible was placed into the furnace at 700^{o}C for 2 hours until constant weight. The resulting content was transferred to a desiccator to cool and weighed again and recorded as weights w4. The difference between weights 3 and 4 was obtained as our %ash content.

2.2.4 % Fixed Carbon (FC)

Fixed carbon was calculated by mass balance using the following formula.

$$\% FC = 100\% - (MC + VM + A) \qquad (1)$$

2.3. Catalyst Preparation

Cow bone sample was properly washed with hot water to remove debris, dirt and fats from the bone. It was oven dried at 105°C for about four (4) days to eliminate moisture present and to dry up some of the fats. It was then calcinated at 800^{o}C in a muffle. The same procedure was also carried for the arowana fish scale.

2.4 Experimental procedure

Slow pyrolysis of the samples were performed in an horizontal reactor (length: 280 mm; i.d.34 mm) in nitrogen as the carrier gas at atmospheric pressure. 15 g of biomass was loaded into the reactor and Nitrogen carrier gas was introduced into the reactor. The starting temperature was ambient room temperature and at a heating rate of 50^{o}C/min. Once final pyrolysis temperature was attained, the reactor was maintained at this temperature for a period of 1 h to ensure that all condensable vapors were collected. A heat exchanger condenser consisting of a thermostatic bath was used to condense the volatile vapor phase which was then collected into a bottle. The procedure was repeated for all the temperatures investigated.

3.0 Results and discussion

3.1 Proximate analysis

Proximate analysis was used to determine the moisture content, volatile matter, fixed carbon content and the ash content of the samples as presented in Table 1.

Table 1. Proximate analysis of samples

Sample	M (%)	VM (%)	FC (%)	Ash (%)
Catholic Vegetable	4.02	79.66	12.76	2.86
Cassava Peel	6.5	76.75	14.22	2.10

3.2 Biomass pyrolysis without catalyst

Figure 1 shows the bio oil yield of the biomass samples at different temperatures and at different particle sizes without the catalyst. The bio oil yield for cassava peels was higher than the oil obtained from catholic vegetable at all temperatures. The yield of bio oil for particle size less than 300µm at 450^{o}C was 20% and 17 % for catholic vegetable and cassava peels respectively. As temperature increased to 700^{o}C, bio oil yield increased to 32% and 24% for catholic vegetable and cassava peels respectively. The bio oil yield at 450^{o}C for catholic vegetable and cassava peels was 18% and 15% respectively for particle size fraction 300-600µm and at 700^{o}C, the yield increased to 30% and 22% respectively. The biggest size fraction investigated gave oil yield of 16% and 9% at 450^{o}C and 26% and 16% at 700^{o}C respectively. The results show that particle size affects the pyrolysis behavior of biomass fuels [23] and that different biomass may have different pyrolysis characteristics such that bio oil yield during pyrolysis will significantly depend on the type of biomass used. However, the significant higher bio oil yield observed for the catholic vegetable might be due to the presence of inherent alkali and alkaline minerals present in the catholic vegetable sample which would catalyze the decomposition reaction during the pyrolysis process as the catalytic role of these inherent minerals in biomass was observed during biomass coal co-combustion [24]. Secondly, it might also be due the difference in textural structure of cellulose, hemicellulose and lignin of the raw material which might result from the milling process.

3.3 Biomass pyrolysis with catalyst

Since the catholic vegetable produced higher yield of bio oil than the cassava peels, catalyst was added to the 300 µm sample in order to further enhance the bio oil yield. Figure 2 shows the catalytic effect of cow bone ash and Arowana fish scale ash on the yield of bio oil from catholic vegetable. For the different catalyst loading investigated, the bio oil produced was higher than the oil produced the sample with catalyst especially at higher temperature and higher catalyst loading. The oil produced from arowana fish scale ash at the catalytic of 1/;15g at 450^{o}C, 550^{o}C and 700^{o}C is 23%, 31% and 42% respectively and they are 2%, 5% and 10% higher than the values obtained at these temperatures without catalyst. As the catalyst loading increased to 2:15g, the quantities of bio oil produced increase to 23%, 31%, and 42 % at 450^{o}C, 550^{o}C and 700^{o}C respectively which was 3%%, 6% and 10% higher than quantity obtained without catalyst. Similar result was obtained as catalyst loading increased to 3:15g, the difference between the oil produced with catalyst and without catalyst at 450^{o}C, 550^{o}C and 700^{o}C were 4, 6, and 10%. However, at 700^{o}C for 3:15g catalyst loading, the same with that of 1.15 g and 2:15g at 700^{o}C suggesting that 700^{o}C is the maximum temperature for the catalytic activity of the fish scale ash.

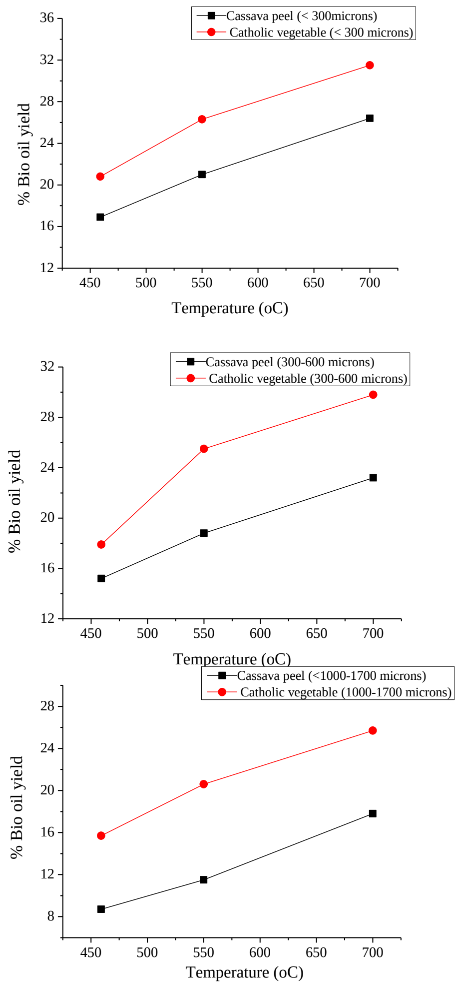

Figure 1. Comparison of bio oil yield from non-catalytic pyrolysis of the biomass samples

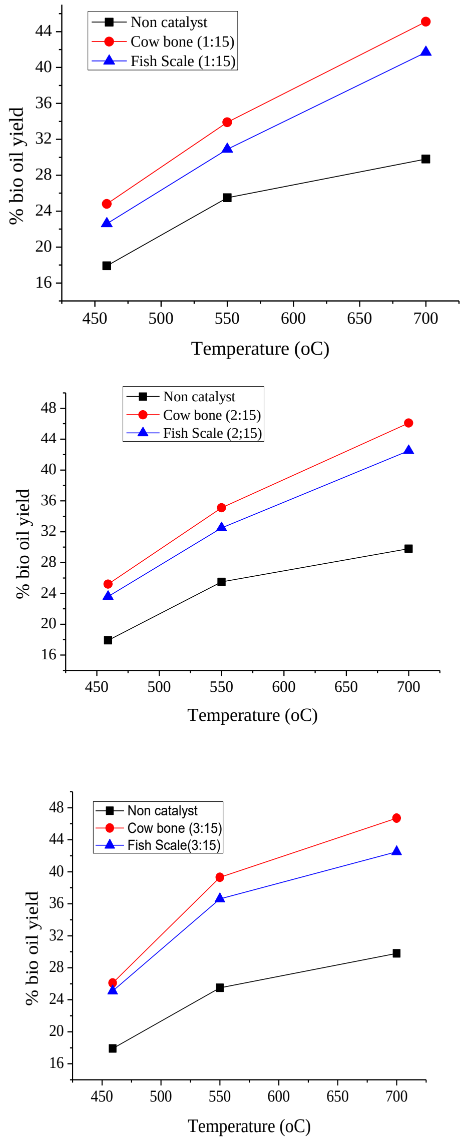

Figure 2. Comparison of the catalytic effect of cow bone and Arowana fish ash on bio oil yield of catholic vegetable for particle size 300µm

Furthermore, for all the temperatures and catalyst loading investigated, the cow bone ash catalyst was found to produce higher bio oil than the Arowana fish scale ash as can be seen in Figure 2. The oils produced from cow bone ash at the catalytic of 1:15 g at 450°C, 550°C and 700°C are 25%, 34% and 45% respectively and they are 4%, 8% and 13% higher than the values obtained at these temperatures without catalyst. As the catalyst loading increased to 2:15g, the quantities of bio oil produced increase to 25%, 35%, and 46 % and the 450°C, 550°C and 700°C respectively which are 4%, 9% and 14% higher than quantity obtained without catalyst. Furthermore, 3:15g gave 5%, 13% and 15% higher yield than bio oil obtained without catalyst. To further investigate which other factors could be responsible for the higher catalytic effect of the cow bone ash on the yield of bio oil, mineral analysis of the ash samples were carried out and the results presented in Table 2. From Table 2, it is shown that the concentration of alkali and alkaline minerals in bone ash are higher than what was found in Arowana fish scale ash. The higher concentration of these is the reason for the higher bio oil yield for the pyrolysis with the cow bone ash. It has been observed by other researchers that alkali and alkaline metals such as Ca, K, Mg, Na catalyzes biomass decomposition [6]

Table 2. Minerals composition of Cow bone ash and Arowana fish scale ash

Elements and symbols	Arowana fish scale ash	Cow bone ash
	Concentration (wt%)	Concentration (wt%)
Calcium, Ca	71.51	70.22
Potassium K	0.91	1.14
Magnesium Mg	0.58	1.13
Sodium Na	0.51	0.67
Aluminum	0.43	0.42
Iron	0.25	0.26

Some properties of the bio oil produced from the non-catalytic process for the two biomass samples were then compared with crude oil in order to obtain some vital information on the possible use of bio oil in the infrastructures of the existing refineries and the results are presented in Table 3.

Table 3. Comparison of physiochemical properties of bio oil produced and crude oil

Bio oil Properties	Catholic vegetable bio oil	Cassava Peels bio oil	Crude oil (light crude
colour	Dark brown	Dark brown	Dark brown
pH	4.4	3.7	4.1
API@60/60°F	40.5	42.0	39.6
Specific Gravity@60/60°F	0.823	0.816	0.827
Density, g/cm^3	0.923	0.816	0.824
Viscosity @40°C, mm^2/sec	0.753	0.827	4.9
Acidity, mg/l	12.50	480.0	0.1

The color of the bio oil from the two samples is dark brown which is the same as that of the crude oil. [19] also reported dark brown color for bio oil produced from slow pyrolysis of palm Empty fruit bunches. From Table 3, it can be seen that the pH of the two samples differs significantly. The pH of the bio oil produced from Catholic vegetable is 4.4 which are closed to the crude oil which has a pH of 4.4, while that from cassava peels is 3.7. The different researchers have reported different pH values of bio oil produced from different biomass samples. For example, Khor et al, [19] reported pH of 3.6 for bio oil produced from slow pyrolysis of palm Empty fruit bunches. Sousa et al, [21] reported 3.8 for bio oil produced from fast pyrolysis of

Elephant grass while Joseph et al [18] reported pH of 5 from bio oil produced from slow pyrolysis of Nigerian yellow and white corn cobs. The results suggest that the pH of bio oil will depend on the type of biomass material. API values of the bio oils are 40.5 and 42.0 for catholic vegetable and cassava peels respectively while that of the crude oil is 39.6. Usually, API value of crude oil of 40 and above is light crude which means the bio oils produced are light crudes. The density of the bio oils produced from catholic vegetable and cassava peels are 0.923g/cm3 and 0.816g/cm3 respectively which that of the crude oil is 0.824g/cm3 as can be seen from Table 3. These values are slightly smaller than the values obtained by other researcher [18, 19, 21). There is significant difference in the acidity value of the two bio oils produced. The catholic vegetable has 12.5 mg/l while the cassava peels has 460 mg/l compared to the crude oil of 0.1mg/1. The higher acidity of the cassava peels may be due to the presence of larger amount of organic acid, phenolic and hydroxyl acids [25] in the bio oil produced compared to that from catholic vegetable. Consequently, the high acidity of the bio oils produced will make the bio oils unsuitable for use in the existing petroleum refineries and therefore must be upgraded in order for them to fit into the existing infrastructure of the refineries.

4.0 Conclusion

Comparison of non-catalytic and catalytic pyrolysis of two biomass samples has been investigated. It was observed that more oil was produced at all temperatures from the catholic vegetable than cassava sample suggesting that biomass type will affect bio oil yield during pyrolysis. In order to enhance the bio oil from the sample that produced more oil at the temperatures considered, ash from natural waste materials was used as catalysts during the pyrolysis process of the two samples. The results show that cow bone ash enhanced oil production than the fish scale ash. This may be due to the higher percentage of alkali and alkaline metals present in the bone ash which would have catalyzed the pyrolysis reaction. Comparing the physiochemical properties of the bio oils produced from the non- catalytic pyrolysis of the two biomass samples with values obtained by other researcher revealed some similarities. The properties have also shown some similarities to the light crude sample suggesting that bio oil has some potential to replace crude oil in the near future if some upgrading is done to reduce the acidity.

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