
Production of Biofuel by Catalytic and Non-Catalyst Pyrolysis of Plantain Stalk

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doi:<https://doi.org/10.37745/ijeer.13/vol12n14669>

Published June 30, 2024

Citation: Dike O.K., Agarry S.E., Ozioma E.P., Bello-Hassan M., and Oluwadamilola O. (2024) Production of Biofuel by Catalytic and Non-Catalyst Pyrolysis of Plantain Stalk, *International Journal of Energy and Environmental Research*, 12 (1), 46-69

ABSTRACT: *The depletion of global fossil fuel reserves and environmental concerns associated with its production are driving the shift towards biomass as a renewable energy source, which can be converted into biofuels and biogas for diverse energy applications. Hence, we conducted pyrolysis experiments on plantain stalk samples to examine the impact of pyrolysis temperature and heating rate on product yields and their chemical compositions. Optimal conditions for maximum bio-oil yield (22%) were identified at a torrefaction pre-treatment temperature of 300°C. The highest biochar yield (16.88%) was achieved at 300°C, while the highest biogas yield (61.85%) was observed at 150°C. Detailed elemental, proximate, and ultimate analyses of the bio-oil were performed, and its chemical composition was analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). The chromatographic and spectroscopic studies confirmed that bio-oil derived from plantain stalk is a promising renewable fuel and chemical feedstock, indicating its potential in sustainable energy applications.*

KEYWORDS: biomass, bio-oil, feedstock, plantain stalk, pyrolysis, bio-oil characterization, renewable energy

INTRODUCTION

The growing depletion of fossil fuels globally is becoming a keen interest for scientists. As cited by (Goyal *et al.*, 2009), Crude oil reserves are decreasing at the rate of 4 billion tons per year and if carried on at this rate with an increase in demand by industries utilizing crude oil, the known oil deposits will be gone by 2052. In Nigeria, over 11.2 billion barrels of crude reserve has been estimated severally to last for a further 31 years. The environmental challenges posed by exploring and exploiting these fossil fuels have drawn the attention of researchers toward renewable energy

as a keen alternative to fuel sources Biomass captures and stores solar energy through photosynthesis in plants. This stored energy is released as heat when biomass is burned. It can be utilized directly or converted into biofuels and biogas. For instance, crops and waste can be processed into fuel or biofuels, while wood waste can be incinerated to generate electricity or transformed into biogas. Comprising carbon and hydrogen, biomass serves as a vital resource for fuel and various industrial applications. Typically, it refers to plant matter grown for biofuel, but it also encompasses plant or animal materials used for producing fibers or chemicals.

Regarding the global issues of sustainable energy and reduction in greenhouse gases, biomass is getting increased attention as a potential source of renewable energy. According to the World Energy Assessment report, 80% of the world's primary energy consumption is contributed by fossil fuel, 14% by renewable energy (Out of which biomass contributes 9.5%), and 6% by nuclear energy. Certainly, among several alternative energy resources, biomass which in the energy production industry refers to living and dead biological materials consisting mainly of cellulose, hemicelluloses, and lignin is seen to play an important role both as chemical feedstock to produce man-made fibers and synthetic rubbers and as an alternative to fossil fuels. Due to these basic facts, investigations on thermo-chemical and bio-chemical conversion technologies for biomass utilization have been conducted worldwide. These include both traditional uses such as a ring for cooking and heating, and modern uses such as producing electricity and steam and liquid biofuels.

Experimental Procedures

MATERIALS AND METHODS

Plantain Stalk

Plantain belongs to Musaceae, the banana family of plants, and it's closely related to the common banana. It is believed to be native to Southeast Asia, they are grown in tropical regions around the world and in a variety of cuisines. Unripe plantains are green to yellow, difficult to peel, and the fruit is hard with a starchy flavor—this is the perfect stage for boiling and frying them. When fully ripe, plantains are black, with a flavor that some people describe as like a banana. Like bananas, plantains are originally from the Southeastern part of Nigeria, however, they are now grown all over the world, including in India, Egypt, Indonesia, and tropical regions of the Americas (Harvard, T. H)

Plantains are large and tend to be tougher than bananas, with much thicker skin. They may be green, yellow, or very dark brown. Plantains are mostly starchy, tough, and not very sweet. They require cooking, as they are not enjoyable to eat raw.



Figure 1: Different representations of plantain and its stalk

Pretreatment of the Biomass

Plantain stalk was obtained from Otuoke market in Bayelsa state. Unwanted particles were removed from the biomass selected to reduce the level of contamination in the pyrolysis products. The feedstock was sun-dried and then oven-dried to reduce the moisture content, and the samples were continuously weighed until the weight became constant.

Characterization of Plantain Stalk

Two (2) grams of crushed plantain stalk particles were measured into a test tube and a syringe was used to add 0.5 ml of sodium hydroxide to it. There was a reaction and the colour changed to yellow indicating the presence of essential oils, which signifies the feasibility of pyrolysis. Also, proximate analysis was done on 20 g of the dried and crushed plantain stalk to determine the moisture content, and the presence of crude fiber, crude protein, crude lipids, and ash. All these were done to ensure that plantain stalk can be used as biomass in the thermochemical conversion process to biofuel.

Pyrolysis

Pyrolysis is a thermo-chemical decomposition process in which organic material is converted into a carbon-rich solid and volatile matter by heating in the absence of oxygen. The solid, termed variously as char, biochar, charcoal, or coke, is generally of high carbon content and may contain around half the total carbon of the original organic matter. The volatiles can be partly condensed to give a liquid fraction leaving a mixture of so-called ‘non-condensable’ gases. The process is simply represented in Figure 2 below.

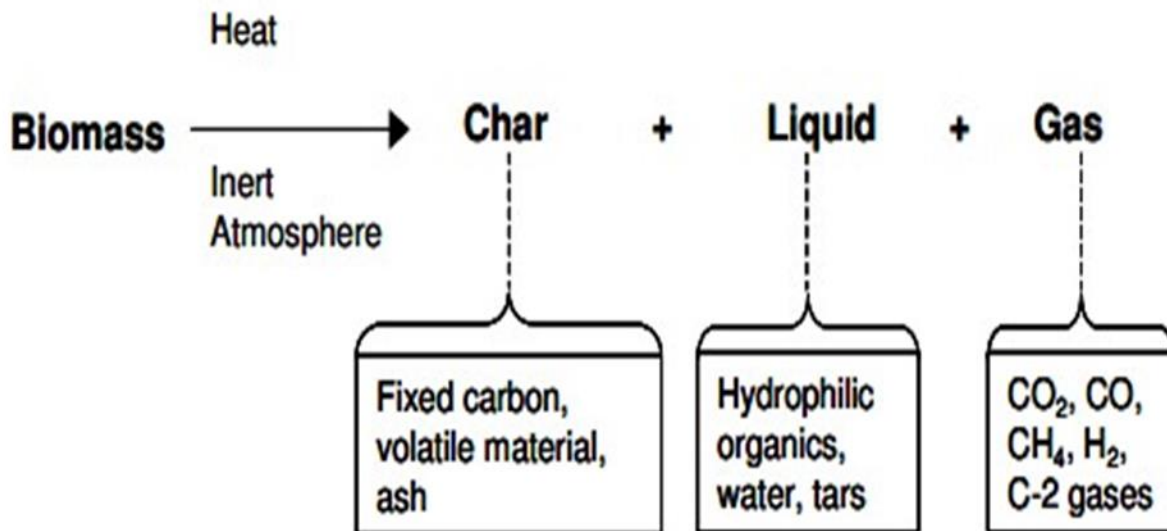


Figure 2: Simple Representation of Pyrolysis Process

Taguchi Experimental Design for the Pyrolysis of Plantain Stalk

Five pyrolysis conditions or factors, each with four levels, were employed in this experiment as shown in Table 1 below. The factors are the pyrolysis temperature, torrefaction, reaction time, particle size, and catalyst. The pyrolysis products consist of the responses

Table 1: Experimental pyrolysis factors and their levels

Symbol	Factors	Levels			
		1	2	3	4
A	Torrefaction	150	200	250	300
B	Temperature (°C)	400	450	500	550
C	Particle Size (mm)	1.18	2.36	3.54	4.72
D	Reaction Time (min)	5	15	25	35
E	Catalyst	0	1	1.5	2.0

A Taguchi L16 (45) orthogonal experimental design was used.

Table 2. $L_{16} (4^5)$ Taguchi orthogonal array experimental design layout

Run	Main Factors									
	A		B		C		D		E	
	Coded	Actual	Coded	Actual	Coded	Actual	Coded	Actual	Coded	Actual
L1	1	150	1	400	1	1.18	1	5	1	0
L2	1	150	2	450	2	2.36	2	15	2	1.0
L3	1	150	3	500	3	3.54	3	25	3	1.5
L4	1	150	4	550	4	4.72	4	35	4	2.0
L5	2	200	1	400	2	2.36	3	25	4	2.0
L6	2	200	2	450	1	1.18	4	35	3	1.5
L7	2	200	3	500	4	4.72	1	5	2	1.0
L8	2	200	4	550	3	3.54	2	15	1	0
L9	3	250	1	400	3	3.54	4	35	2	1.0
L10	3	250	2	450	4	4.72	3	25	1	0
L11	3	250	3	500	1	1.18	2	15	4	2.0
L12	3	250	4	550	2	2.36	1	5	3	1.5
L13	4	300	1	400	4	4.72	2	15	3	1.5
L14	4	300	2	450	3	3.54	1	5	4	2.0
L15	4	300	3	500	2	2.36	4	35	1	0
L16	4	300	4	550	1	1.18	3	25	2	1.0

The Taguchi $L_{16} (4^5)$ experimental design entails sixteen runs of experiments that require five factors or parameters, each with four levels. The columns 1, 2, 3, 4, and 5 of the L_{16} orthogonal array were correspondingly assigned to the torrefaction (A), temperature (B), particle size (C), reaction time (D), and catalyst (E).

The pyrolysis experiment was conducted in line with the design provided in Table 2. The experimental setup for the pyrolysis is given in Figure 3 below.



Figure 3: Experimental setup

The furnace was heated to a temperature of 450 °C which is above the required minimum temperature so that after putting the plantain stalk in the retort and placing it in the furnace the required temperature will still be maintained. The sample to be pyrolyzed was weighed before the commencement of each pyrolysis run and after. The retort was properly packed to prevent leakages and placed in the metal furnace which was connected to the condensate receiver through a galvanized iron pipe. The condensate receiver was placed inside the ice bath containing the ice block. The ice block aids the vapour condensation of the pyrolysis product from the retort. The condensate receiver was again connected to the gas collection unit through a rubber hose and tightened at both ends with clips. The gas collection unit has one inlet pipe which the impure gas from the condensate receiver flows through and two outlet pipes. The water inside the gas collection unit filters impure gases and the pressure of the gas displaces some quantity of water through one of the outlet pipes. The filtered gas was tapped from the other outlet pipe into the gas cylinder. The products (biochar, bio-oil, and biogas) of the pyrolysis were collected, weighed, and recorded. The flow diagram of the process is provided in Figure 4 Below.

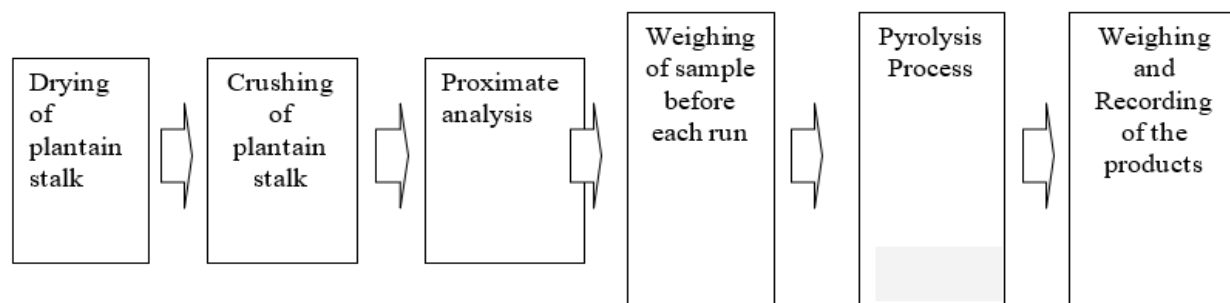


Figure 4: The flow diagram of the process

Characterization of biofuel using GC/MS

The physicochemical properties (flashpoint, pour point, cloud point, density, viscosity, and pH) of the bio-oil were determined. The components or composition of the pyrolysis products were determined using the GC/MS. All these were carried out at the Chemical Engineering Laboratory of Rivers State University, Nigeria.

Sample Analysis (GC-MS)

10 ml of the sample was added into an amber glass bottle. The sample was stirred. 300 µg/ml of surrogate (1-chlorooctadecane) standard was added to the sample. 30 ml of dichloromethane (DCM) was added to the sample as extracting solvent and the bottle containing the sample was corked very tight and transferred to a mechanical shaker. The sample was agitated between 5 to 6 h at room temperature using a mechanical shaker. After agitation, the sample was allowed to settle for 1 h and then filtered through 110 mm filter paper into a clean beaker. The filtrate was allowed to concentrate to 1 ml by evaporation overnight in a fume cupboard.

Data Analysis

Signal-to-noise ratio (S/NR) and analysis of variance (ANOVA) were applied to decide the optimum or maximum levels of each of the factors and the significance of the factors, respectively. These were computed for the bio-oil, biochar, and biogas yields, respectively. The S/NR was computed for the pyrolysis products yield using the criterion “highest-is-best” quality characteristics, and it is determined using:

$$\left(\frac{S}{N}\right)_{HB} = \frac{-10 \log \sum_{i=1}^n \left(\frac{1}{y}\right)^2}{n}$$

where y is the output or response, and n is the number of experiments conducted per experimental run

Results

Characteristics of the Plantain Stalk

Proximate Analysis

The proximate analysis results are shown in Table 3.

Table 3: Proximate analysis result of the Plantain stalk sample

Volatle Matter %	Ash content %	Moisture content %	HH Value (Btu/gm)
18.19	4.16	9.14	141.826

Table 3 shows that the moisture content in plantain stalk was 9.14%.

Bridgwater *et al.* (1999) suggested that the biomass moisture content should be less than 11% for an efficient pyrolysis process. The plantain stalk shows low amounts of volatile matter (18.19%). This indicates that there are small amounts of cellulose and hemicellulose in the plantain stalk. The presence of volatile matter in biomass determines the thermal decomposition or combustibility of the biomass (Shadangi *et al.*, 2014). Biomass with higher volatile matter can be more reactive with lower volatile content. That is, during pyrolysis, biomass with more volatile matter produces more liquid and gaseous fuel (Shadangi *et al.*, 2014). Ash content in the plantain stalk is low with a value of 4.16%. (Table 3) which depicts its suitability as a raw material for bio-oil production. For pyrolysis, biomass with high ash content is faced with a reduction in thermal decomposition rate and an increased chance of slag accumulation as well as erosion in the pyrolysis reactor (Varma *et al.*, 2017). The plantain stalk estimated higher heating value (HHV) is 141.826 Btu/gm.

Ultimate Analysis

The elemental analysis of the maize-cob-derived bio-oil is shown in Table 4.

Table 4: Ultimate analysis result of the bio-oil sample

PARAMETERS	RESULTS			SD		
	RUN 1	RUN 8	RUN 16	RUN 1	RUN 8	RUN 16
Carbon %	51.50	47.90	32.50	<77.0	<77.0	<77.0
Nitrogen %	5.69	7.86	4.96	<12	<12	<12
Sulphur %	1.55	0.41	0.31	<0.5	<0.5	<0.5
Oxygen %	9.19	9.98	7.55	11.0max	11.0 max	11.0max
Hydrogen %	11.50	11.70	10.90	12.0max	12.0max	12.0max

The results for the elemental analysis of plantain stalk-derived-bio-oil as presented in Table 4 indicate that for bio-oil, the presence of a catalyst in run L16 reduced the amount of carbon, nitrogen, sulphur, oxygen, and hydrogen contents present in the oil as compared to the amount of these elements present in the bio-oil obtained from run L1 and run L8 without the presence of a catalyst. The decreased sulphur, oxygen, and nitrogen contents imply that the plantain derived-bio-oil will have a reduced pollutant effect, which indicates that it is eco-friendly (Chukwuneke *et al.*, 2019). The reduction in the nitrogen, oxygen, and sulfur contents could be due to the reason that the catalyst has helped to partition the nitrogen, oxygen, and sulfur into the biogas primarily as NO, NO₂, CO, CO₂, and H₂S along with water production (Mullen *et al.*, 2010; Ilknur *et al.*, 2012; Ali *et al.*, 2016).

Characterization of Bio-Oil Produced from Pyrolysis of Plantain Stalk**Physical characterization**

The bio-oil that was selected for characterization was the one obtained at the optimum pyrolysis process conditions. The physical characterization results are provided in Table 5.

Table 5. Physical properties of bio-oil produced from plantain stalk

Properties	Value	ASTM D6751	ASTM D7544-12	
			Grade G	Grade D
Cloud point (°C)	-14	>-6	Report	Report
Pour point (°C)	-8 to -17	>-14	≤-9	≤-9
Flash point (°C)	118-120	>130	≥45	≥45
Kinematic Viscosity@40°C (cSt)	31	1.9 – 6	≤125	≤125
Density @ 25 °C (kg/m ³)	0.89-1.09	1.100-1.300	1.1-1.3	1.1-1.3
pH	5.85	-		

The cloud point is the temperature at which the smallest cluster of hydrocarbon crystals begins to occur in the liquid oil upon cooling under prescribed conditions (Ige *et al.*, 2021). Fuel in an environment below a cloud point tends to solidify and form hydrocarbon crystals, which inhibits engine parts movement and thus alters its working efficiency (Khan *et al.*, 2016). According to the results in Table 4.7, the plantain stalk derived-bio-oil cloud point was obtained as -14 °C. This value is in tandem with the biofuel standard based on ASTM. The pour point is the lowest or minimum temperature at which the oil will cease to flow when cooled in a standard apparatus at prescribed conditions (Khan *et al.* 2016). The pour point is a criterion used for the low-temperature performance of a fuel. The pour point of the plantain stalk derived-bio-oil was found to be in the range of -8 to -17 °C. This value agrees with the range of -15 °C - (-10 °C) specified by ASTM. The value also compared well with the value of -15 °C obtained for bio-oil derived from plastic waste pyrolysis by Khan *et al.* (2016). Flash point is the lowest temperature at which a liquid oil can vaporize to form an ignitable mixture in the air (Khan *et al.*, 2016). The higher the flash point, the lower the presence of highly volatile compounds, and thus the safer the oil handling as the possibility of accidental vapor ignition will be reduced. The plantain stalk derived-bio-oil flash point was obtained to be in the range of +118-120 °C which is low. The flash point value obtained for this oil is relatively less than the 130 °C specified by ASTM D6751 and greater than the 45 °C specified for conventional fuel Grade G and D by ASTM D7544-12 and thus indicates that plantain stalk-derived-bio-oil storage is safe and stable at room temperature. The bio-oil kinematic viscosity obtained at 40 C which is a property that defines the fuel flow characteristics was found to be 31 cSt. This value is higher than the value specified by ASTM D6751 for biofuel but less than the maximum value specified for Grade G and D conventional fuel by ASTM D7544-12. High viscosity of bio-oil will inhibit its free flow. Fuel with high viscosity causes several problems such as contamination of lubricating oil, incomplete combustion, and deposits formation at the injection nozzle tip (Ige *et al.*, 2021). The difference in these values could be a result of water content variation present in the bio-oils, and the increase in water content in bio-oils leads to a reduction of the kinematic viscosity (Bardalai *et al.*, 2016). The density of the bi-oil was obtained as 1.09 kg/m³. This value falls within the density range (0.964-1.300 kg/m³) of many bio-oils reported in the literature (Ali *et al.*, 2016; Bardalai *et al.*, 2016; Ige *et al.*, 2021). However, bio-oil's oxygen content and high viscosity may cause it to exhibit instability during storage (Zhang *et al.*, 2011).

According to the results in Table 4.7, the bio-oil pH was obtained to be 5.85. This reveals that the bio-oil is slightly acidic in nature.

Taguchi's analysis of the effects of pyrolysis factors on the bio-oil, biochar, and biogas yields of pyrolyzed plantain stalk

According to the Taguchi experimental design for the pyrolysis of plantain stalk, the bio-oil, biochar, and biogas yields obtained are given in Table 6.

Table 6. Experimental $L_{16} (4^5)$ orthogonal array and the experimental results

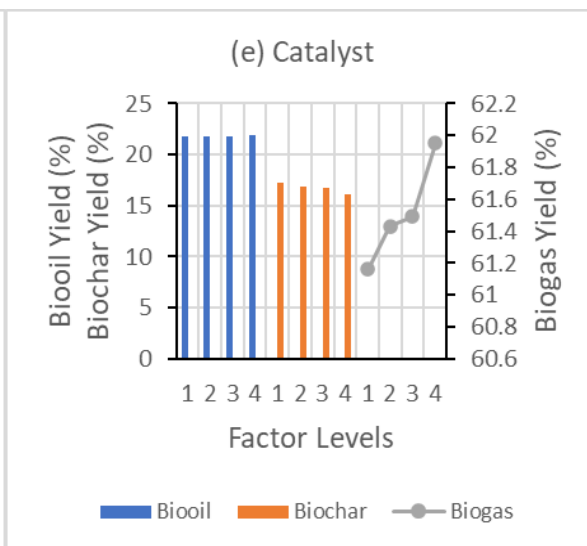
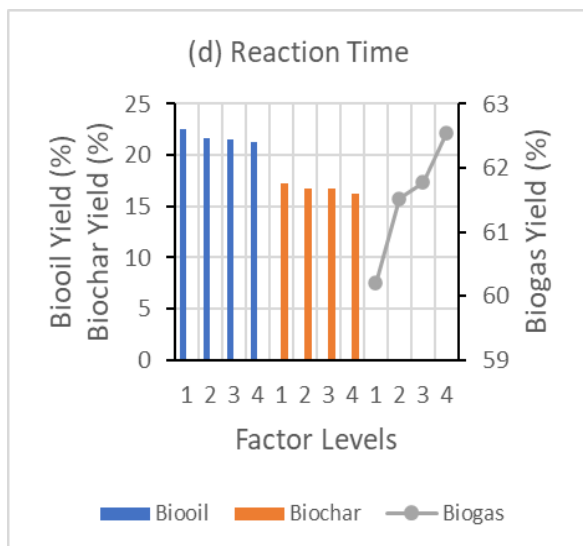
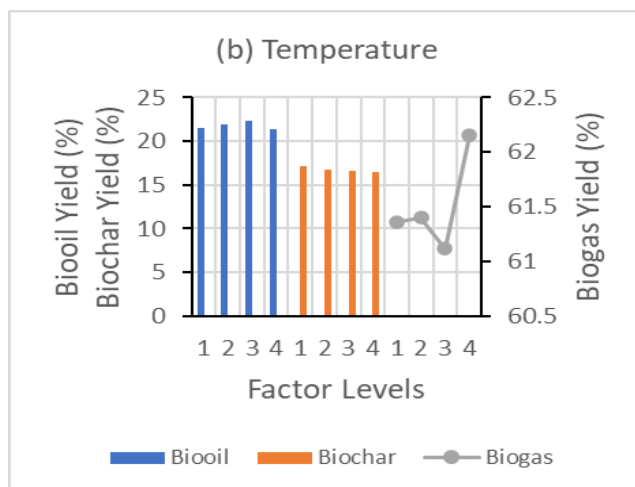
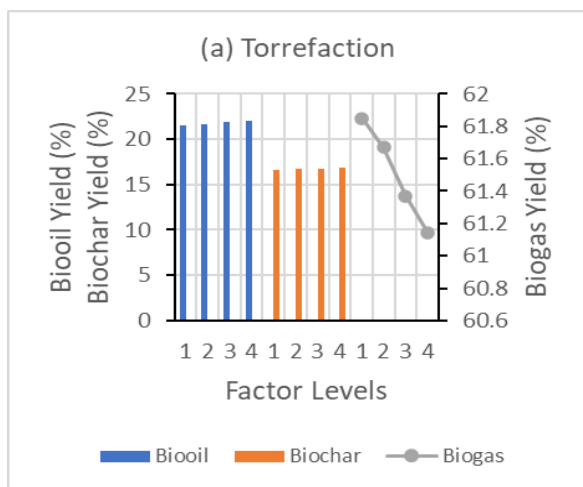
Run	Main Factors					Biooil Yield (%)		Biochar Yield (%)		Biogas Yield (%)	
	A	B	C	D	E	Average	S/NR	Average	S/NR	Average	S/NR
						Value		Value		Value	
L1	1	1	1	1	1	22.72	7.45	17.98	6.77	59.30	10.23
L2	1	2	2	2	2	21.83	7.34	16.70	6.56	61.47	10.33
L3	1	3	3	3	3	21.43	7.28	16.47	6.52	62.10	10.36
L4	1	4	4	4	4	20.13	7.10	15.36	6.32	64.51	10.47
L5	2	1	2	3	4	21.45	7.29	16.52	6.53	62.03	10.36
L6	2	2	1	4	3	22.08	7.37	16.07	6.45	61.85	10.35
L7	2	3	4	1	2	22.31	7.40	17.27	6.66	60.42	10.28
L8	2	4	3	2	1	20.76	7.19	16.85	6.59	62.39	10.38
L9	3	1	3	4	2	20.55	7.16	16.86	6.59	62.59	10.39
L10	3	2	4	3	1	21.03	7.23	17.27	6.66	61.70	10.34
L11	3	3	1	2	4	23.40	7.54	15.90	6.42	60.70	10.30
L12	3	4	2	1	3	22.48	7.42	17.02	6.62	60.50	10.29
L13	4	1	4	2	3	21.04	7.23	17.45	6.69	61.51	10.34
L14	4	2	3	1	4	22.56	7.43	16.88	6.59	60.56	10.29
L15	4	3	2	4	1	22.14	7.38	16.62	6.55	61.24	10.32
L16	4	4	1	3	2	22.20	7.39	16.55	6.54	61.25	10.32

In estimating the main effect of factor, A (torrefaction) on the response variables (biooil yield, biochar yield and biogas yield), the total average value of three experimentally observed responses

at level 1 of factor A was divided by 3 to attain the average value for the response at level 1 of factor A. In the same vein, the average responses at levels 2, 3, and 4 were achieved. The estimated effects of the factors are provided in Table 7. These effects are graphically illustrated as presented in Figure 6.

Table 7. Estimated main effects of factors on the pyrolysis products' yields of plantain stalk

Pyrolysis Factors	Bio-oil yield (%)			
	1	2	3	4
Torrefaction (A)	21.53	21.65	21.87	22.00
Temperature (B)	21.51	21.88	22.39	21.41
Particle Size (C)	22.61	21.98	21.33	21.13
Reaction Time (D)	22.59	21.70	21.53	21.23
Catalyst (E)	21.74	21.80	21.83	21.89
	Bio-char yield (%)			
Torrefaction (A)	16.63	16.68	16.76	16.88
Temperature (B)	17.20	16.73	16.57	16.45
Particle Size (C)	16.63	16.72	16.77	16.84
Reaction Time (D)	17.29	16.73	16.70	16.23
Catalyst (E)	17.18	16.85	16.75	16.17
	Biogas yield (%)			
Torrefaction (A)	61.85	61.67	61.37	61.14
Temperature (B)	61.36	61.40	61.12	62.16
Particle Size (C)	60.78	61.31	61.91	62.04
Reaction Time (D)	60.20	61.52	61.77	62.55
Catalyst (E)	61.16	61.43	61.49	61.95



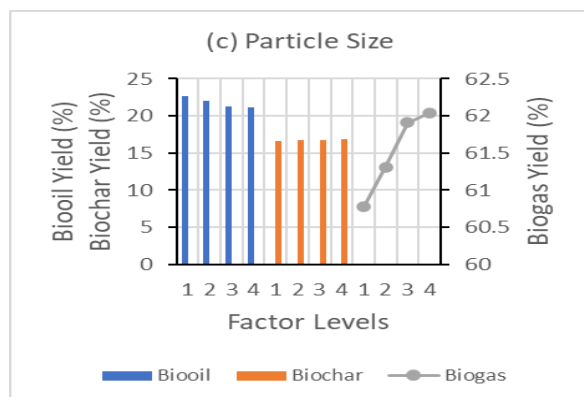


Figure 5: Estimated main effects of different pyrolysis factors at varying factors' levels on biooil, biochar and biogas yields obtained from plantain stalk pyrolysis: (a) torrefaction (b) temperature (c) particle size (d) reaction time (e) catalyst

As shown in Figure 5(a), as the pre-treated torrefaction temperature increased from level 1 (150°C) to level 4 (300°C), the bio-oil yield increased up to 250°C, and at a torrefaction temperature of 300°C, it decreased, while the bio-char and biogas yields generally decreased. That is, the yields of bio-oil, bio-char, and biogas change at different temperatures of torrefaction due to the biomass heating at different stages of temperature stage (Klaas *et al.*, 2020). The highest bio-oil yield of 22% was achieved at pre-treated torrefaction temperature of 300 °C, while the highest yield of bio-char (16.88%) and the highest yield of biogas (61.85%) was obtained at 300 °C and 150 °C, respectively. Klaas *et al.* (2020) have reported for the pyrolysis of corncob a similar observation of an increased bio-char yield and a decreased biogas yield with respect to increasing pre-treatment torrefaction temperature.

Figure 5(b) shows the effect of pyrolysis temperature on the yields of biooil, biochar, and biogas. The results indicate that increase in the temperature of pyrolysis from level 1 (400 °C) to level 4 (600 °C) gave rise to an increase in the bio-oil percentage yield up till 550 °C (which ranged from 21.51 to 22.39%) and at 600 °C, it slightly decreased to 21.41%. Also, there is a general increase in the biogas percentage yield (ranging from 61.74 to 62.62%) and a decrease in the bio-char percentage yield (ranging from 16.91 to 16.15%) as the pyrolysis temperature increased from 400 to 600 °C. The high biochar yield at lower temperature reveals that the biomass has only been partially pyrolyzed (Angin 2013). The increase in the percentage yield of bio-oil may be due to increased heat decomposition and increased secondary reactions (like cracking, re-condensation and re-polymerization) of chars with volatiles (Adelawon *et al.*, 2022). Similar observation of a decreased bio-char yield due to rise in pyrolysis temperature has been reported for the pyrolysis of

agricultural biomass such as palm kernel shell (Zaman *et al.*, 2018), corn stover (Soka *et al.*, 2020) and maize-cob (Adelawon *et al.*, 2022). Zaman *et al.* (2018), Soka *et al.* (2020) and Adelawon *et al.* (2022) have respectively reported a similar increase in bio-oil yield due to increase in pyrolysis temperature in the pyrolysis of palm kernel shell, corn stover and maize-cob, while the observation of a rise in biogas yield due to increased pyrolysis temperature in this study is perfectly in agreement with the observation reported by (Soka *et al.*, 2020; Adelawon *et al.*, 2022) for the pyrolysis of corn stover and maize-cob, respectively. The increase in biogas percentage yield could be due to the secondary decomposition of the pyrolysis vapors and the bio-char (solid residue) at higher temperatures (Ilknur *et al.*, 2012; Adelawon *et al.*, 2022).

The effect of plantain stalk particle size (1.18-4.72 mm) on the biooil, biochar and biogas yields obtained from the pyrolysis of plantain stalk is presented in Figure 5(c). For bio-oil, bio-char, and biogas products, the results obtained reveals that as the particle size increases from small size of level 1 (1.18 mm) to large size of level 4 (4.72 mm), the bio-char and biogas percentage yields increased, while the bio-oil percentage yield decreased. The increased bio-char percentage yield and the reduced bio-oil percentage yield due to increase in the particle size from small to large may be due to increase in the internal heating rate reduction within the particles as the size increases. That is, as the size of the plantain stalk particles gradually increases, so also the particles' mean internal temperature (MIT) decreases (i.e. reduces or becomes lower) and hence, will undergo low heating (i.e. heat up more slowly) and low rate of reaction thereby resulting in decreased decomposition and formation of more residues of solids (bio-chars) and decreased percentage yield of bio-oil (Zaman *et al.*, 2018; Adelawon *et al.*, 2022). When the size of the particle is small, the MIT of the particles will relatively be high with higher heating rate and higher rate of reaction leading to higher decomposition with subsequent biochar formation reduction and increased percentage yield of bio-oil. The reduction in bio-oil percentage yield observed in this study due to increasing plantain stalk particle size is well in agreement with what has been observed for the pyrolysis of palm kernel shell (Zaman *et al.*, 2018) and maize-cob (Adelawon *et al.*, 2022), respectively. Also, the observed increase in both the percentage yields of biogas and bio-char due to increasing plantain stalk particle size was found to be in concordance with what has been reported for the pyrolysis of maize stalk (Ali *et al.* 2016) and maize-cob (Adelawon *et al.*, 2022), respectively. Meanwhile, it was reported by Yorgun *et al.*, (2015) for the slow pyrolysis of paulownia wood that there was no significant particle size effect on the yields of biochar and biogas produced.

Figure 5(d) depicts the effect of reaction time on the plantain stalk pyrolysis products (biooil, biochar and biogas). The results show that with an increasing reaction time from level 1 (5 min) to level 4 (35 min), there is a corresponding decrease in both the bio-oil and bio-char percentage

yields, while the biogas percentage yield increased. (Uzun *et al.*, 2013; Adelawon *et al.*, 2022) have respectively reported for pine sawdust and maize-cob similar observations of a decreased bio-oil and bio-char percentage yields, as well as an increased percentage yield of biogas due to increasing reaction time.

The effect of the catalyst on the bio-oil, bio-char, and biogas percentage yields of pyrolyzed plantain stalks is shown in Figure 5(e). It is seen that both the bio-oil and biogas percentage yields increased as the amount of added catalyst increased, while the percentage yield of bio-char decreased. Fan *et al.* (2020) reported a decrease in the yields of liquid oil and char as well as an increase in biogas yield obtained from the catalytic pyrolysis of both pinewood and peanut shell when potassium carbonate (K_2CO_3) was used as a catalyst. Okekunle *et al.* (2021) have also reported that the yields of bio-char increased with increasing amount of sodium carbonate catalyst while the biogas decreased with respect to increasing quantity of sodium carbonate amount during the pyrolysis of African Copaiba Balsam (*Daniellia Oliveri*) sawdust.

ANOVA and Signal to Noise Ratio Analysis of Bio-Oil, Bio-Char and Biogas Yields

The pre-treatment torrefaction temperature, pyrolysis temperature, plantain stalk particle size, reaction time, and catalyst were studied for their effects on the pyrolysis products (bio-oil, bio-char and biogas yields) of plantain stalk. Table 8 shows the ANOVA and the percentage contribution of each factor for the bio-oil, bio-char, and biogas percentage yields.

Table 8. ANOVA results obtained for the bio-oil, bio-char and biogas percentage yields derived from plantain stalk pyrolysis

Source	Bio-oil Yield (%)			
	Sum of Squares	DF	Mean of Squares	Percentage Contribution
Model	11.89	15	0.79	-
A	0.51	3	0.17	4.30
B	2.26	3	0.75	18.97
C	5.36	3	1.79	45.10
D	3.66	3	1.22	30.74
E	0.11	3	0.035	0.89

Bio-char Yield (%)				
Source	Sum of Squares	DF	Mean of Squares	Percentage Contribution
Model	5.96	15	0.40	-
A	0.14	3	0.047	2.36
B	1.33	3	0.44	22.25
C	0.096	3	0.032	1.60
D	2.26	3	0.75	37.85
E	2.14	3	0.71	35.93
Biogas Yield (%)				
Model	Sum of Squares	DF	Mean of Squares	Percentage Contribution
Model	20.50	15	1.37	
A	1.18	3	0.39	5.74
B	2.47	3	0.82	12.06
C	4.06	3	1.35	19.82
D	11.49	3	3.83	56.05
E	1.30	3	0.43	6.33

The percent contributions of the factors are shown in Table 8. Percent contribution indicates the relative power of a factor to reduce variation (Agarry and Ogunleye, 2015). For a factor with a high percent contribution, a small variation will have a great influence on the performance. According to Table 8 for bio-oil percentage yield, plantain stalk particle size was found to be the major factor affecting the percentage yield of bio-oil (45.10%), reaction time was found to be the second ranking factor (30.74%) and relatively followed by pyrolysis temperature (18.97%). The percentage contributions of torrefaction and catalyst are much lower, being 4.30% and 0.89%, respectively. Also, according to Table 8 for bio-char percentage yield, reaction time was found to be the major factor affecting the percentage yield of bio-char (37.85%), catalyst was found to be the second ranking factor (35.93%) and relatively followed by pyrolysis temperature (22.25%). The percentage contributions of torrefaction and particle size are much lower, being 2.36% and 1.60%, respectively. Furthermore, based on Table 8 for the percentage yield of biogas, reaction time was observed to be the major factor that affected the percentage yield of biogas (56.05%), particle size was seen to be the second ranking factor (19.82%) and closely followed by pyrolysis temperature (12.06%). The percentage contributions of catalyst and torrefaction are much lower, being 6.33% and 5.74%, respectively. Furthermore, the relative influence or impact of each pyrolysis factor was also determined by the maximum and minimum S/Ns' differential of the levels (δ) value as presented in Table 9

Table 9. Mean S/N ratio for the bio-oil, bio-char and biogas percentage yields

Factors	Biooil Yield (%)				$\delta = \text{Maximum} - \text{Minimum}$
	1	2	3	4	
Torrefaction (A)	7.29	7.32	7.34	7.36*	0.07
Temperature (B)	7.28	7.34	7.40*	7.28	0.12
Particle Size (C)	7.44*	7.36	7.27	7.24	0.20
Reaction Time (D)	7.43*	7.33	7.30	7.25	0.18
Catalyst (E)	7.31	7.32	7.31	7.33*	0.02
Biochar (%)					
Torrefaction (A)	6.54	6.56	6.57	6.59*	0.05
Temperature (B)	6.65*	6.57	6.54	6.52	0.13
Particle Size (C)	6.55	6.57	6.57	6.58*	0.03
Reaction Time (D)	6.66*	6.57	6.56	6.48	0.18
Catalyst (E)	6.64*	6.59	6.57	6.47	0.17
Biogas Yield (%)					
Torrefaction (A)	10.35	10.35	10.34	10.39*	0.05
Temperature (B)	10.33	10.33	10.32	10.37*	0.05
Particle Size (C)	10.30	10.33	10.36	10.36*	0.06
Reaction Time (D)	10.28	10.34	10.35	10.38*	0.10
Catalyst (E)	10.32	10.33	10.34	10.36*	0.04

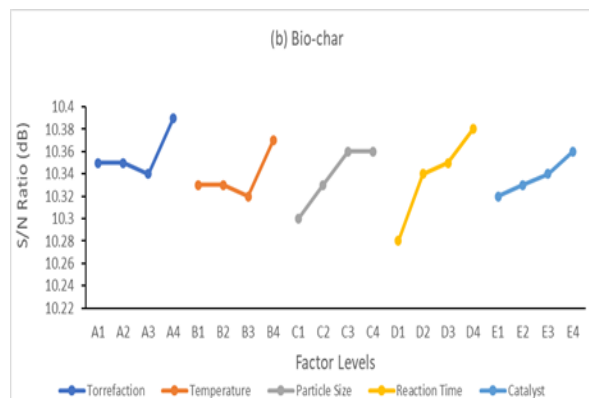
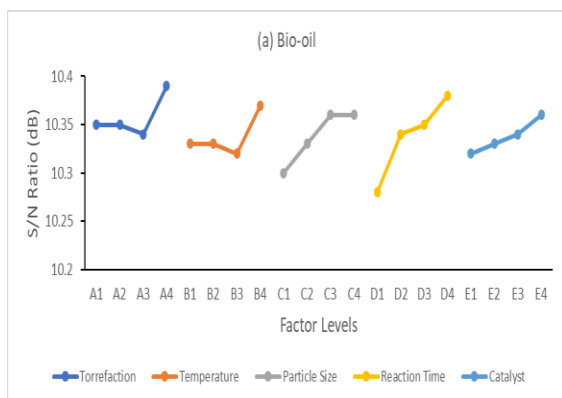
*Optimum level

The value or magnitude of the δ is very relevant for the ranking of the effects of the factors (i.e., from the strongest to the weakest) on the bio-oil, bio-char and biogas yields. The larger the

magnitude of δ , the greater the relative effect or impact (Agarry *et al.*, 2020). Among the investigated factors' effects on the percentage yield of bio-oil, factor C (particle size) elicited a stronger effect than the rest of the factors, with its δ value of 0.20 being the highest. This was closely followed by factor D (reaction time) with δ value of 0.18, factor B (temperature) with δ value of 0.12, factor A (torrefaction) with δ value of 0.05, and factor E (catalyst) with δ value of 0.02. That is, the ranking of the factors' effects is as follows: C > D > B > A > E. Similarly, as shown in Table 4.5, the effect of the factors on bio-char percentage yield is ranked as follows: D ($\delta = 0.18$) > E ($\delta = 0.17$) > B ($\delta = 0.13$) > A ($\delta = 0.05$) > C ($\delta = 0.03$); while the effect of the factors on biogas percentage yield is also ranked in the following order: D ($\delta = 0.10$) > C ($\delta = 0.06$) > B and A ($\delta = 0.05$) > E ($\delta = 0.04$). Also, it was observed that the sequence of the factors' effect rankings based on the δ values was consistent with the ranking due to the percentage contribution presented in Table 7.

Parametric Optimization of Bio-Oil, Bio-Char and Biogas Yields

The plantain stalk pyrolysis experimental results provided in Table 6 showed that the 23.40% maximum bio-oil percentage yield was gotten in run L11, where the experimental pyrolysis conditions were a combination of A3 (torrefaction, 250 °C), B3 (temperature, 500 °C), C1 (particle size, 1.18 mm), D2 (reaction time, 15 min) and E (catalyst, 2.0 g). Meanwhile, 20.13% minimum bio-oil percentage yield was achieved at run L4 with the combination of factors' levels of A1 (torrefaction, 150 °C), B4 (temperature, 550 °C), C4 (particle size, 4.72 mm), D4 (reaction time, 35 min), and E4 (catalyst, 2.0 g). Nonetheless, based on the mean S/N ratio determined for each factor's level (as shown in Table 9 and Figure 7 (a)), the optimum or maximum set of factor levels to optimize or maximize bio-oil percentage yield were chosen to be levels A4, B3, C1, D1 and E4. A higher S/N ratio value implies a higher percentage yield.



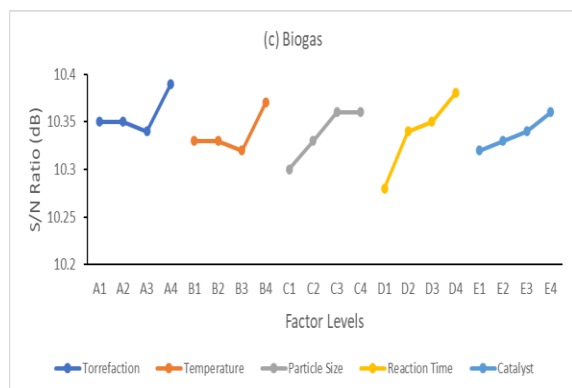


Figure 7 (a) S/N ratio plot for bio-oil percentage yield at various factor levels. (b) S/N ratio plot for bio-char at various factor levels. (c) S/N ratio plot for biogas at various factor levels.

Confirmation Test

In this study, after determining the optimum conditions and predicting the response under these conditions, we designed and conducted a new experiment with the optimum levels of the factors considered. The result is presented in Table 10.

Table 10: Results of confirmation experiment

	Optimal Process Parameters	
	Experimental	Predicted
Level	A4B3C1D1E4	A4B3C1D1E4
Bio-oil percentage yield	23.85	24.44
S/N (dB)	7.59	7.66
Level	A4B1C4D1E1	A4B1C4D1E1
Bio-char percentage yield	17.22	17.78
S/N (dB)	6.65	6.74
Level	A4B4C4D4E4	A4B4C4D4E4
Biogas percentage yield	63.10	63.80
S/N (dB)	10.41	10.44

From the laboratory validation experiment conducted at these predicted optimum process conditions, the following percentage yield of products was obtained: bio-oil (23.85%), bio-char (17.22%), and biogas (63.10%). The error in percentage between the predicted and validated experimental values was found to be -2.47, -0.34, and -1.11 for bio-oil, bio-char, and biogas, respectively. These results revealed that there are no significant differences between the predicted and experimentally observed values.

GC-MS characterization of bio-oil

Chemical characterization of bio-oil is pertinent and useful such that these oils can be treated as mixtures of a few groups of organic compounds rather than as mixtures of larger groups of different organic compounds (Yorgun and Yildiz 2015). The chemical content of bio-oil was determined using GC-MS. Among the many peaks displayed in the GC-MS chromatogram (Figure 8), the most abundant spectra with higher intensities have been identified in comparison with the spectrum found in the WILEY spectrum library.

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Injection Date   : 11/02/2022 02:48:13 PM
Sample Name     : Bio-oil Run 8 No Catalyst
Acq. operator  : ARAL575
Location       : Vial 3
                Inj : 1
                Inj Volume : 1 µl

Method         : C:/HPCHEM/1/METHODS/PAH-2.M
Last Changed   : 11/01/2022 10:41:57 AM by ARAL575
  
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PAH Method 2

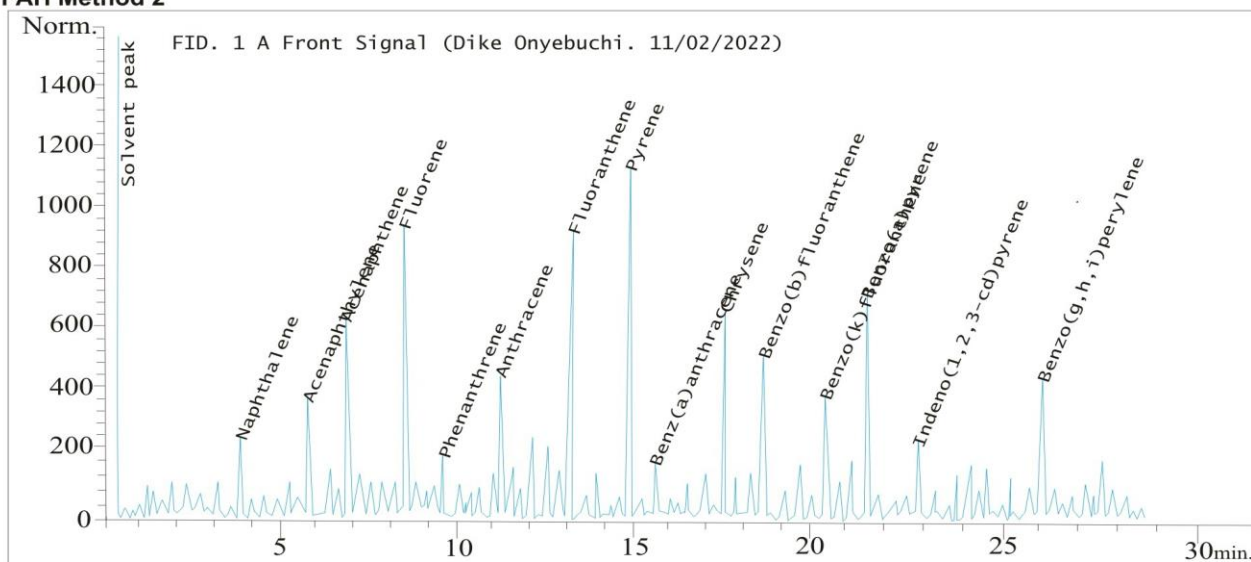


Figure 8: Chromatograph

The identified peak areas which indicate the major organic components are listed in Table 11.

Table 11: GC-MS analysis of the major components of pyrolyzed oil from plantain stalk.

Main components	RT/min	Area w/%
Naphthalene	6.354	64.71648
Acenaphthylene	6.553	93.93485
Acenaphthene	6.635	46.71250
Fluorene	7.562	79.83642
Phenanthrene	9.327	52.53192
Anthracene	9.402	83.83169
Fluoranthene	11.940	46.46713
Pyrene	12.232	37.38461
Benz (a) anthracene	15.138	91.34087
Chrysene	15.282	63.34910
Benzo (b) fluoranthene	17.598	75.75211
Benzo (k) fluoranthene	18.105	44.43109
Benzo (a) pyrene	20.249	35.93584
Indeno (1,2,3-cd) pyrene	20.580	81.83150
Dibenz (a, h) anthracene	20.869	-
Benzo (g, h, i) perylene	21.356	53.75311

Table 11 shows that the bio-oil from plantain stalk biomass contained aromatic compounds, mostly polycyclic aromatic hydrocarbons of which acenaphthene accounted for the largest proportion of bio-oil (93.93% of the total peak area detected followed by Benz (a) anthracene (91.34%).

CONCLUSION

In this study, the Pyrolysis of plantain stalk gave three main fuel types: Biochar (the solid constituent), Bio-oil (the liquid constituent), and Biogas. The gas obtained was confirmed to be a cooking Gas. It is possible to vary the product distribution between char, liquid, and gas by choice of process type and operating conditions. The variation of the changes in temperature, time, and particle size affected the yield of the products. Specifically, as the temperature increases, the biochar yield reduces, consequently increasing the yield of both bio-oil and biogas. The flash point of bio-oil produced is higher than that of petroleum diesel as seen in Table 5 making it less of a fire hazard.

The Major compounds found in the bio-oil obtained from the pyrolysis of plantain stalk were mostly polycyclic aromatic hydrocarbons of which acenaphthene accounted for the largest proportion of bio-oil (93.93% of the total peak area detected followed by Benz (a) anthracene (91.34%).

REFERENCES

- Adelawon, B. O., Latinwo, G. K., Eboibi, B. E., Agbede, O. O., and Agarry, S. E. (2022). Comparison of the slow, fast, and flash pyrolysis of recycled maize-cob biomass waste, box-benhken process optimization and characterization studies for the thermal fast pyrolysis production of bio-energy. *Chemical Engineering Communications*, 209: 1246 – 1276.
- Agarry, S. E. and Ogunleye, O. O. (2015). Bioadsorption of 2,6-Dichlorophenol from aqueous solution onto plantain and pineapple peels mixture used as adsorbent: optimization studies based on Taguchi method, Batch Equilibrium, and Kinetic Modelling. *Chemistry and Materials Research*, 7(3): 1-15.
- Ali N, Saleem M, Shahzad K, Hussain S, Chughtai A. 2016. Effect of operating parameters on production of bio-oil from fast pyrolysis of maize stalk in bubbling fluidized bed reactor. *Polish J Chem Technol*. 18 (3): 88-96.
- Angin D. 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource Technol*. 128: 593-597.
- Bardalai M, Mahanta DK. 2016. Characterisation of the pyrolysis oil derived from bael shell (aegle marmelos). *Environ Eng Res*. 21 (2): 180-187.
- Bridgwater AV, Meier D, Radlein D. 1999. An overview of fast pyrolysis of biomass. *Organic Geochem*. 30: 1479-1493.
- Chukwunke JL, Ewulonu MC, Chukwujike IC, Okolie PC. 2019. Physico-chemical analysis of pyrolyzed bio-oil from *swietenia macrophylla* (mahogany) wood. *Heliyon*. 5 (6): e01790, 1-6.
- Fan, H., Chang, X., Wang, J., and Zhang, Z. (2020). Catalytic pyrolysis of agricultural and forestry wastes in a fixed-bed reactor using K₂CO₃ as the catalyst. *Waste Management and Research* 38 (1): 78-87.
- Harvard T.H. Chan School of Public Health. (n.d.). The Nutrition Source - Bananas and Plantains. Retrieved from Harvard T.H. Chan School of Public Health
- Ige AR, Elinge CM, Aliyu M, Gwani M, Lawal HG. 2021. Optimization and characterization of bio-oil produced from rice husk using surface response methodology. *Acta Chemica Malaysia* 5: 10-17.
- İlknur D, Alper E, Sevgi Ş. 2012. Bio-oil production from pyrolysis of corncob (*Zea mays* L.). *Biomass and Bioenergy*. 36: 43-49.
- Khan MZH, Sultana M, Al-Mamun MR, Hasan MR. 2016. Pyrolytic waste plastic oil and its diesel blend: fuel characterization. *J Environ and Public Health*. 2016: Article ID 7869080, 1-6. <http://dx.doi.org/10.1155/2016/7869080>.

- Klaas M, Greenhalf C, Ouadi M, Jahangiri H, Hornung A, Briens C, Berruti F. 2020. The effect of torrefaction pre-treatment on the pyrolysis of corncobs. *Results in Eng.* 7 (100165): 1-7.
- Mullen CA, Boateng AA, Goldberg NM, Lima IM, Laird DA, Hicks KB. 2010. Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. *Biomass Bioenergy.* 34(1): 67–74.
- Okekunle, P. O., O. Olasupo, A., & Adeyemi, I. A. (2021). Effect of Temperature and Catalyst on Biofuel Yields from Pyrolysis of African Copaiba Balsam (*Daniellia Oliveri*) Sawdust. *Covenant Journal of Engineering Technology* 5(1): 29-36.
- Goyal, H.B.; Seal, D.; Saxena, R.C (2009). Bio-fuels from thermochemical conversion of renewable energy
- Shadangi KP, Mohanty K. 2014. Thermal and catalytic pyrolysis of Karanja seed to produce liquid fuel. *Fuel.* 115: 434-442.
- Soka O, Oyekola S. 2020. Feasibility assessment of the production of char using the slow pyrolysis process. *Heliyon.* 6 (e04346): 1-6.
- Uzun BB, Kanmaz G. 2013. Effect of operating parameters on bio-fuel production from waste furniture sawdust. *Waste Manage Res.* 31: 361-368.
- Varma AK, Mondal P. 2017. Pyrolysis of sugarcane bagasse in semi batch reactor: Effects of process parameters on product yields and characterization of products. *Ind Crops Prod.* 95: 704–717.
- Yorguna S, Yıldız D. 2015. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. *J Anal Appl Pyrol.* 114: 68-78.
- Zaman KK, Balasundram V, Ibrahim N, Samsudin MDM, Kasmani RMD., Abd Hamid MK, Hasbullah H. 2018. Effect of particle size and temperature on pyrolysis of palm kernel shell. *Int J Eng Technol.* 7 (4.35): 118-124.
- Zhang C, Zhang R, Li X, Li Y, Shi W, Ren X, Xu X. 2011. Bench-scale fluidized-bed fast pyrolysis of peanut shell for bio-oil production. *AIChE.* 30 (1): 11-18.