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OPTIMIZATION AND CHARACTERIZATION OF BIO-OIL PRODUCED BY PYROLYSIS OF COCONUT SHELL THROUGH RESPONSE SURFACE METHODOLOGY

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Abstract:
The use of biomass for biofuel production is gaining popularity as a waste-management option. However, data on the characterization of bio-oils derived from the pyrolysis of coconut shells is lacking. Therefore, the effects of pyrolysis variables, such as reaction temperature, reaction time, and particle size on bio-oil yield were investigated in this study. At optimum conditions of 700°C temperature, 100min. reaction time, and 1.00mm particle size, the optimized bio-oil yield was 44.25wt percent. The viscosity, density, pH, moisture content, ash content, and heating value were all determined to be 10.15cSt, 1.09g/cm3, 0.05wt percent, and 40.00MJ-kg^{-1}, respectively. The results were found to be within the range of results documented in previous literature for biomass-based bio-oils. The Fourier Transform Infrared FT-IR and Gas Chromatography Mass Spectrometry GC-MS results of the bio-oil samples revealed the presence of high concentrations of phenols, oxygenated compounds, acids, and other compounds that are useful as industrial chemicals and flammable gases. This study establishes that coconut shells can be used as an alternative fuel source which can be a major raw material in the petrochemical industry.

Key words: *Coconut shell; Temperature; Bio-oil; Particle size; Reaction time.*

INTRODUCTION

The role of fossil fuels will be significant, but new resources and renewable energy will dominate them. One technology that can be used to deal with this is pyrolysis, which uses organic waste (biomass) as raw material.

There is an increasing demand for energy in various places worldwide owing to urban migration, population growth, and good standard of living. Fossil fuels have negative impacts caused by their use for different purposes, which have created more hazards to the environment owing to environmental factors (Jagadesan *et al*. 2020). This has led to increased demand for renewable resources worldwide (Chukwuneke *et al*. 2019).

The benefits of biomass as a tool to provide sufficient energy have aroused interest as a better option for renewable energy (Zhao and Li 2016, Chin *et al*. 2015). Biomass, in general, has the potential to replace most other fuels or sources of energy, because biomass fuels play an important role in providing the required energy needs.

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Pyrolysis can be referred as a thermo-chemical conversion of the biomass through direct thermal decomposition in complete or in complete absence of oxygen which generates three significant products consisting of solid, liquid and gas which are biochar, bio-oil and non- condensable gases respectively (Bridgwater 2012). Pyrolysis technology can be used to utilise organic waste and contribute to the creation of a better environment through the creation of value-added products thereby ensuring zero waste generation.

Bio-oil produced by pyrolysis is a dark-brown organic liquid with a burly bitter smell (Faisal *et al.* 2011), and it typically possesses lower hydrogen and carbon contents and high oxygen contents when compared with fossil fuels (Faisal *et al.* (2011), Josilaine *et al*. (2013), Stefanidis *et al.* (2013). It is a thermodynamically unbalanced liquid but wealthy in functional groups (Faisal *et al.* 2011). Bio-oil, when subjected to combustion tests, has high burning effectiveness which makes it a viable fuel (Faisal *et al.* 2011). Different biomass stocks would give varying yields and bio-oil properties.

Previous studies on coconut shell for bio-oil production have seen enough research; however, no work has been done on enhancing coconut shell bio-oil production utilizing surface response approach. To save money, coconut shell bio-oil was produced without the use of a catalyst or a carrier gas to test the production and quality of the bio-oil. The objectives of this study were to investigate the effect of surface response methodology for the prediction of bio-oil yield and evaluate the physicochemical parameters of the experimental bio-oil from the predicted pyrolysis parameters. Furthermore, the above-mentioned parameters are commonly used to evaluate the quality of bio-oil. However, no literature review was found detailing the quality of bio-oil obtained from non-catalytic pyrolysis process.

MATERIALS AND METHODS

Biomass Samples Preparation

Coconut shell was collected at Alafara Ologuneru Ibadan, Oyo State, Nigeria, in the Ido Local Government Area. The coconut shells were pulverized and cleaned with distilled water to eliminate contaminants before being dried for 24 hours at 105°C in the oven. The pulverized biomass was dried and stored in airtight containers until it was needed for use (Kasim *et al.* 2018).

Reactor Design

The stainless-steel reactor (height: 570mm, diameter: 260mm) was used in this experiment, had a feeder header (height: 48mm, diameter: 70mm) at the top and a char removal outlet (diameter: 100mm) at the bottom as shown in Fig. 2. As the pilot plant's phase, a rectangular iron rod was fastened to the reactor. Two halves hexagonal stainless-steel pipe (diameter: 10mm, total length: 1840mm) inserted within the reactor in u-shape for uniform and faster heating (bending radius: 43mm).

The reactor has a fixed stock capacity of 1Kg and a 1kW electrical heater, it was coupled to a glassware condenser for the condensation process.

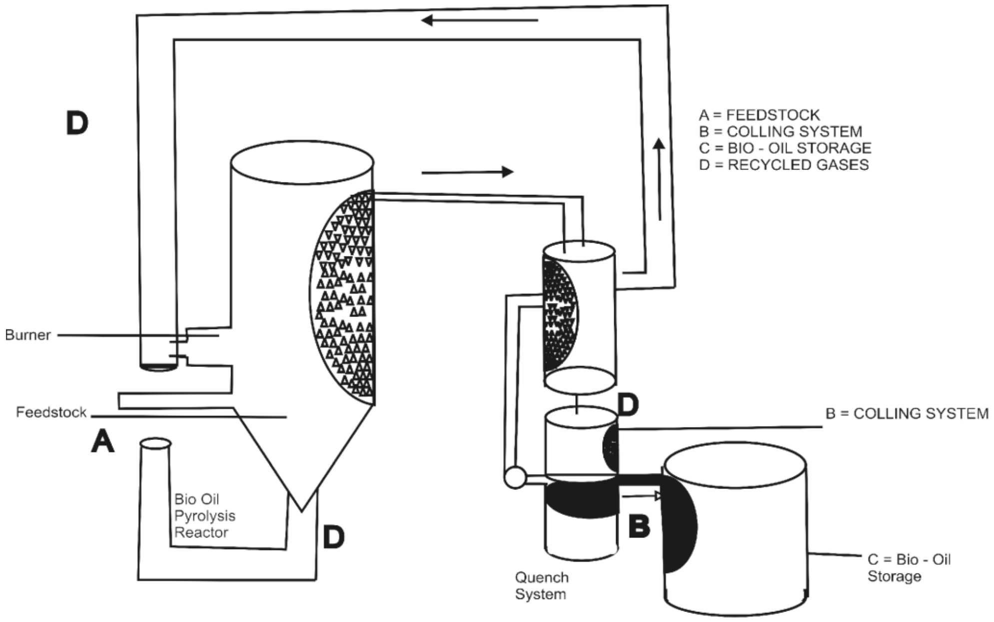


Fig. 1.
Schematic of Pyrolysis Reactor
Source: Adegoke and Ogunsanwo, 2011.

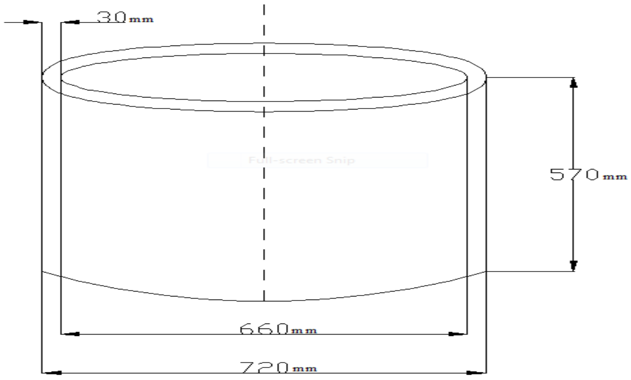


Fig. 2.
Schematic Dimension of the reactor.

Sample Preparation

The coconut shells (1kg) were fed into a stainless-steel fixed bed reactor connected to condenser to produce pyrolytic bio-oil (Fig. 1). The reactor was connected to a condenser filled with 1kg of coconut shells. The evolving gases were distilled into bio-oil in the condenser and collected in a conical flask. Pyrolysis temperature of 500-700°C with a processing time of 40-100 minutes, 1 atm pressure and heating rate of 100°C/min was used to pyrolyze coconut shells.

The solid catalyst particles were not loaded in the fabricated fixed bed reactor, and there is no inert gas to scavenge oxygen in the system. This was done to measure the reactor's efficiency in terms of yield and quality of bio-oil produced without the use of a catalyst or inert gas to save money. After pyrolysing the fed materials, the reactor was allowed to cool naturally. The biochar was then released out of the reactor, and liquid from the reservoir was collected and measured. Bio-oil yield was calculated following the procedures that have been used by Ogunsanwo and Adegoke (2022).

$$\text{Bio-oil Yield } (\%) = \frac{\text{weight of liquid produced}}{\text{weight of incipient pyrolysis material}} \text{ x } 100 \tag{1}$$

$$Solid \text{ Yield } (\%) = \frac{\text{weight. of solid produced}}{\text{weight of incipient pyrolysis material}} \text{ x } 100 \tag{2}$$

$$\text{Non Condensable Gases} = 100 - (\text{Solid Yield} + \text{Liquid Yield}) \tag{3}$$

Experimental Design

The optimization experiment was conducted using Minitab 17 statistical software and response surface methods (Box-Behnken) at a D 0.05 (95 percent confidence level) (Ogala and Ige 2019). Temperature, particle size, and time were chosen as independent variables since they are all important factors in pyrolysis. The runs were completely randomized to obtain a total of 30 runs and to determine the efficiency and long-term viability of the optimal parameters.

Table 1 shows the factors and levels of the variables that were chosen. Response surface regression was used to assess the experimental data using the second-order polynomial model provided by (Aydın and Aksoy 2009) Eq. (4).

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} Xi^2 + \sum_{i>j}^{k} . \sum_{j}^{k} \beta_{ij} \, X_i X_j + e \tag{4}$$

where: Y is the percentage of bio-oil yield; X_i and X_j are coded independent factors; β_o, β_i, β_{ii}, and β_{ij} are regression coefficients for constant, linear, quadratic, and interaction terms, respectively; k is the number of factors studied as well as optimized; and e is the experimental error ascribed to Y.

Table 1

Optimization Processes Variables

Factor	Lower Level	Upper Level
Particle Size (mm)	1.00	4.00
Temperature (°C)	500	700
Time (min)	40	100

Source: Field data, 2022.

Validation of the Predicted Optimum Pyrolysis Process Conditions

To validate the predicted optimum pyrolysis process conditions, coconut shell biomass pyrolysis experiment was conducted at the predicted optimum process conditions. The experimentally observed percentage yield of the bio-oil pyrolysis product was recorded and was used for oil characterization. These recorded values were compared with the predicted values to check the model validity. The Equation (5) provided by Agarry and Ogunleye (2012) was employed to estimate the percentage error (% E) that exists between the experimental observed value and the predicted theoretical value.

$$\%Er = \frac{\mathrm{Ev} - \mathrm{Pv}}{Pv} \times 100 \tag{5}$$

where: Pv is the predicted theoretical value and Ev is the experimental observed value.

Analysis of Raw Materials

Lignocellulosic composition analysis

The method of Mahyati *et al* (2013) was used to analyze lignin and cellulose. A combination containing 1g of dried sample (a) and 150 mL of demineralized water was heated for 1 hour in the oil bath at 100°C. The residue was rinsed with hot demineralized water after the mixture was filtered (300mL). The residue was oven dried until the weight remained consistent (b).

The residue was combined with 150mL of 1 N H_2SO_4 and heated for one hour in an oil bath at 100°C. The mixture was filtered, rinsed with 300mL of de-mineralized water before being dried (c). The dried residue was steeped in 10mL of 72 percent H2SO4 for 4 hours at room temperature.

Thereafter, 150mL of 1 N H_2SO_4 was added to the mixture, which was then refluxed for 1 hour in the oil bath. The material was rinsed with 400 mL demineralized water oven at 105°C and weighed until the weight remained constant (d). Finally, the residual sample was heated until it turned into ash and weighed (e). The percentage of hemicellulose, cellulose and lignin was calculated as follows:

$$\%\ hemicellulose = \frac{(c-b)}{a} \times 100\% \tag{6}$$

$$\%\ cellulose = \frac{(d-c)}{a} \times 100\% \tag{7}$$

$$\%\ lignin = \frac{(e-d)}{a} \times 100\% \tag{8}$$

Proximate and Ultimate Analysis

The proximate analysis (ash, volatile matter, moisture content, and fixed carbon) were evaluated according to ASTM standard. The element analyzer (CHNS analyzer ASTM D5291 technique) was used to determine the final analysis of the raw feedstock and biochar samples, and the oxygen content was estimated according to Sallau *et al.* (2021).

Analysis of Bio-oil

Physico-chemical and Fuel Properties of the Bio-oil

The experimental bio-oil yield obtained using response surface approach was assessed for its physico-chemical and fuel qualities. ASTM standards were used to determine density (ASTM D4052), kinematic viscosity (ASTM D445), pour point (ASTM D97), calorific value (ASTM D240), flash point, and pH (ASTM E70).

FTIR (Fourier Transform Infrared Spectroscopy)

The infrared spectrum of coconut husk biofuel was measured in AVATAR 330. Fourier Transform Infrared Spectrophotometer (FT-IR). Fourier Transform Infrared Spectroscopy (FT-IR) was performed at the Umaru Musa Yar'adua University Central Laboratory, Katsina State, Nigeria.

GC-MS (Gas Chromatography Mass Spectrometry)

The samples were examined for volatile chemicals with a 7820A gas chromatograph and a 5975C inert mass spectrometer (with triple axis detector) equipped with an electron-impact source (Agilent Technologies). HP-5 capillary column coated with 5% Phenyl Methyl Siloxane (30m length x 0.32mm diameter x 0.25m film thickness) served as the stationary phase for compound separation (Agilent Technologies). Helium (He) was employed as the carrier gas, with a constant flow rate of 1.6mL/min, a nominal pressure of 2.84 psi, and an average velocity of 46cm/sec. 1 liter of each sample was injected in split less mode at 260 degrees Celsius. At 0.50 minute, the purge flow was 21.5mL/min, for a total flow of 25.8mL/min; gas saver mode was turned on. The oven was set to 60 degrees for 1 minute, then ramped up at 4 degrees per minute to 110 degrees for 3 minutes, then 8 degrees per minute to 260 degrees for 5 minutes, and 10 degrees per minute to 300 degrees for 10 minutes (12min). With a 3-minute solvent delay, the run time was 56.25 minutes. The mass spectrometer was run in electron-impact ionization mode at 70 eV, with 230°C for the ion source, 150°C for the quadrupole, and 280°C for the transfer line.

Statistical Analysis

Graph Pad Prism® (Version 6.04) was used to compute the average of all the parameters evaluated using one-way analysis of variance (ANOVA), and the findings were given as mean SEM.

RESULTS AND DISCUSSION

Table 2

The lignocellulosic content, proximate and ultimate analysis of coconut shell

Property	**Coconut Shell**
Lignocellulosic Content (wt %)	
Cellulose	18.28±0.03
Hemicellulose	48.31±0.50
Lignin	22.50±0.10
Proximate Analysis (wt %)	
Ash Content	1.40±0.20
Moisture Content	6.83±0.12
Volatile Matter	74.27±0.01
Fixed Carbon	17.50±0.54
Ultimate Analysis (wt %)	
C	44.94±0.23
H	5.51±0.01
O	40.67±0.03
N	4.28±0.24
S	0.18±0.50

Data are means of three replicates (n = 3) ± SD using Graph Pad Prism, CS: Coconut shell
Source: Field data, 2022.

The lignocelluloses values of the raw coconut shell are 18.28wt% of cellulose, 48.31wt% hemicelluloses and 22.50wt% lignin as shown in Table 2. The results are consistent with previous study on rice husks, with 33.2 wt percent cellulose, 35.3 wt percent hemicelluloses, and 19.6 wt percent lignin, as reported by Awoyale and Lokhart (2021). This compares favorably with groundnut shell lignocellulose values of 34 wt percent cellulose, 46 wt percent hemicelluloses, and 28 wt percent lignin reported by Ogunsuyi and Adejumobi, (2020).

High cellulose content with low lignin content is a highly desirable quality in the conversion of lignocellulosic biomass for bio-oil production (Ogunsuyi and Adejumobi 2004).

Table 2 shows the proximate and elemental value of the coconut shell used for this study. The volatile matter obtained for the samples are lower than the result of the finding reported by Lasode *et al.* (2014) and

Prins *et al.* (2006), where the studies reported 82.3wt% for teak dust and 79.0wt% for Switchgrass dust, respectively. The results of ultimate analysis of the coconut shell gave 44.94%, 5.51%, 40.67%, 4.28% and 0.18% for carbon, hydrogen, oxygen, nitrogen, and Sulphur content respectively. The result of the analyses showed that coconut shell investigated could serve as precursors for thermo-chemical process. The analysis of the raw material used before bio-oil production provides some novelty. The effect and process ratio of the bio-oil was investigated as critical values obtained were presented in Tables 2 above.

Table 3

Experimental Design Matrix and Results of Coconut Shell (Pyrolysis Yield) from the Experimental Runs

Run Order	P. Size (mm)	Time (mins)	Temp. (°C)	Bio-oil Yield (%)
1	4	70	600	39.33
2	2.5	70	600	42.72
3	4	100	600	39.5
4	1	40	600	40.81
5	4	70	500	37.89
6	2.5	70	600	42.71
7	2.5	100	700	46.22
8	2.5	100	700	46.2
9	4	70	500	37.92
10	1	100	600	41.1
11	1	70	500	38.49
12	2.5	40	500	40.3
13	4	70	700	40.88
14	4	70	700	40.9
15	2.5	70	600	42.7
16	2.5	70	600	42.69
17	2.5	70	600	42.72
18	1	70	700	42.5
19	2.5	100	500	40.61
20	1	70	500	38.2
21	4	40	600	40.71
22	1	40	600	40.8
23	2.5	40	500	40.32
24	4	40	600	40.7
25	4	100	600	39.51
26	1	70	700	42.51
27	2.5	100	500	40.6
28	2.5	70	600	42.69
29	2.5	40	700	41.7
30	2.5	40	700	41.68

Source: Field data, 2022.

Table 4

Result of Variance for Groundnut Shell Bio-oil yield (%)

Source	DF	AdjSS	Adj MS	F-Value	P-Value
Model	9	36.116	4.01291	1.02	0.002
Linear	3	23.452	7.81737	1.99	0.148
particle size (P)	1	8.180	8.17960	2.08	0.165
temperature (T)	1	6.452	6.45160	1.64	0.215
time (S)	1	8.821	8.82090	2.24	0.150

Square	3	10.998	3.66612	0.93	0.443
particle size *particle size(A)	1	0.008	0.00821	0.00	0.964
Temperature *temperature (B)	1	6.330	6.32985	1.61	0.219
Time *time (C)	1	5.441	5.44051	1.38	0.253
2-Way Interaction	3	1.666	0.55523	0.14	0.934
particle size *temperature (D)	1	0.684	0.68445	0.17	0.681
particle size *time (E)	1	0.001	0.00125	0.00	0.986
Temperature *time (F)	1	0.980	0.98000	0.25	0.623
Error	20	78.649	3.93245		
Lack-of-Fit	3	11.242	3.74730	0.95	0.441
Pure Error	17	12.407	3.96513		
Total	29	114.765			

Source: Field data, 2022.
DF = degree of freedom, Adj SS = adjusted sum of squares, Adj MS = adjusted mean squares, F = F –statistics, P = p-value, and S = statistically significant
Regression Equation in Uncoded Units
Bio-oil Yield = 81.8 - 1.70P - 0.1178T - 0.178S+ 0.015A + 0.000093B+ 0.000954C + 0.00195D - 0.0003E + 0.000117F

ANALYSIS OF VARIANCE

Model: These tests whether the terms in the model have any effect on the response; for regression model to be significant (P< 0.05). The P-value observed was (P = 0.002) which is a clear indication that at least one of the terms in the model has an impact on the mean response. The model is further broken into different orders of terms namely, linear, square, and interaction effect.

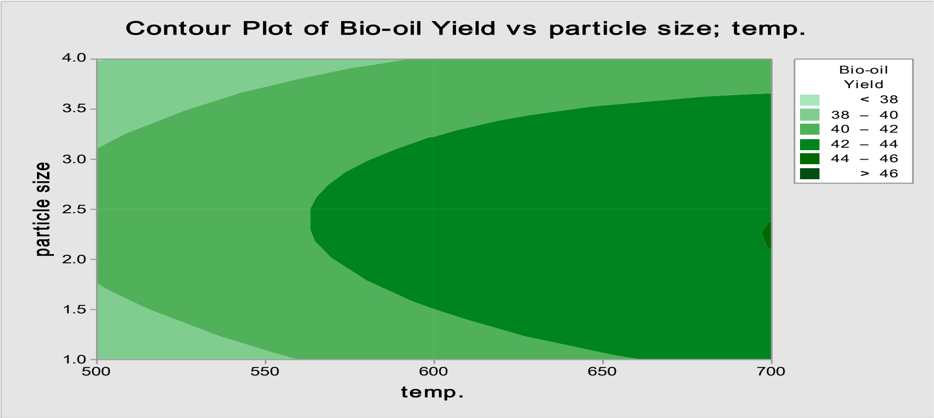
Linear effect: for temperature (P=0.148) is greater than 0.05. Therefore, temperature has no linear effect on the model. Also, P-value for particle size (P=0.165) is greater than (P< 0.05) and time (P=0.150) is greater than (P< 0.05) which shows that time has no linear effect on the model and particle size has no linear effect on the model.

Squared effects: Squared terms are used to evaluate whether there is curvature in the response surface. Therefore, there is significant evidence of a quadratic effect. The individual p-values for temp*temp, particle size*particle size and time*time and are0.964, 0.219, 0.253.

Interaction effects: The p-value of 0.934 is more than 0.05; therefore, there is no significant evidence of interaction effects. The temperature by time interaction is less than 0.05. Therefore, there is a significant interaction effect. That is, the effect of temperature on reaction yield depends on the time as shown in Table 4.

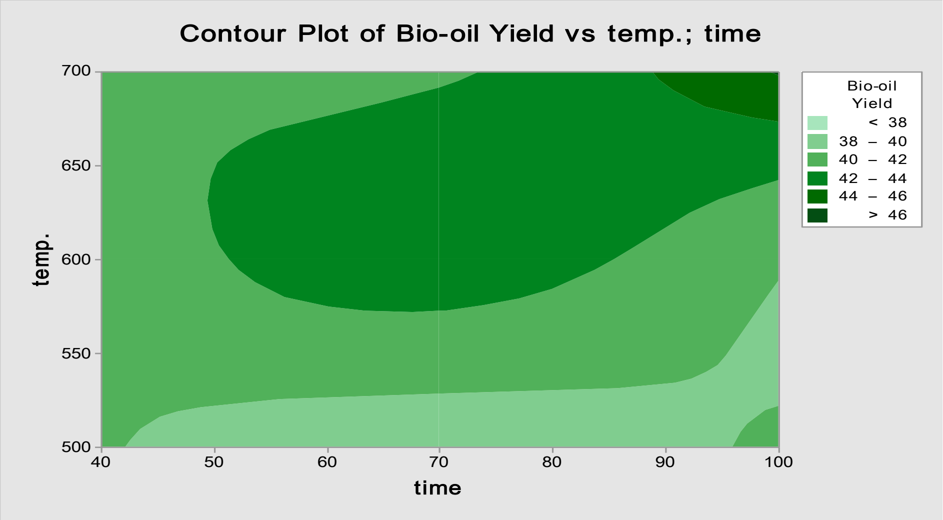
S	R^2	R^2(adj)	R^2 (pred)
1.98304	67.47%	80.63%	74.46%

For the pyrolysis data, 67.47 % of the variation in yield is explained by model, the predicted R is 74.46%, and the adjusted R is 80.63 %. The contour plots were shown in Fig.3 to 4.



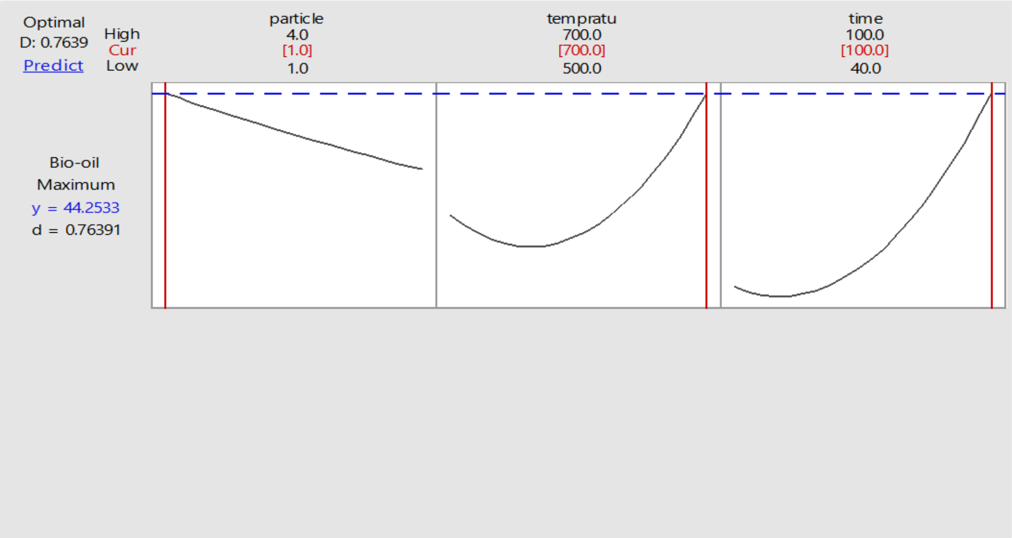
Source: Field data

Fig. 3.
Contour plot of bio-oil yield on time versus temperature when particle size remained constant for coconut shell.



Source: Field data, 2022

Fig. 4.
Contour plot of bio-oil yield on particle size and particle size when temperature held constant for coconut shell.



Source: Field data, 2022

Fig. 5.
Optimization Plot for Coconut Shell.

Minitab 17 statistical software was used to investigate bio-oil yield optimization. Table 4 shows three optimal variables obtained from the 30 optimization runs depicted in Fig. 5. Justifiable experimental runs conducted at the levels of the process variables resulted in a bio-oil yield of 44.25 percent for coconut shell. Although the one-sample t-test shows that the empirical yield is significantly lower than the model prediction, the two are very close, with a difference of less than 1%. This also suggests that the empirical model derived from the response surface design is highly reliable and provides an excellent representation of the process. It is worth noting that higher yields can be obtained by optimizing the various variables.

Process optimization was conducted to determine the optimal percentage of bio-oil yield. Bio-oil yield of 44.25% for coconut shell occurs at a temperature of 500°C, particle size of 1.00mm and time of 40.00 minutes were obtained as optimal conditions suggested as shown in Fig. 5. Confirmation runs were conducted with the above conditions and gave 44.43% for coconut shell. It was indicated that the experimental values obtained were in good agreement with the values predicted from the model which recorded small error between the predicted and the actual value which was only 0.40%.

It can be observed that the bio-oil yield (44.25%) obtained from the fast pyrolysis of coconut shell biomass waste in this study is greater than the bio-oil yield obtained from groundnut shell and groundnut peels (16.3% and 11.7%) by Ogunsuyi and Abimbola (2020); groundnut shell (25%) by Radhakrishnan and

Gnanamoorthi (2015) as well as obtained from corncob (20.5%; 22.2%; 26.44%) by Ceranic *et al*. (2016), Ates and Isikdag (2009), and Ilknur *et al*. (2012).

The differences observed for the percent bio-oil yield of coconut shell and other agricultural biomass may be due to the variety of feed biomass, type of pyrolysis, type of reactor utilized, process conditions, and differences in the quantity of biomass compositions (such as cellulose, hemicellulose and lignin) (Adelawon *et al*. 2021).

Table 5

Physico-chemical analysis of bio-oil

Property	**Coconut Shell**
Ash Content (%)	0.05±0.01
Moisture Content (%)	15.00±0.10
Acid Value	9.00±0.50
Density (g/cm^3)	1.09±0.01
Kinematic Viscosity (cSt)	14.15±0.20
Flash Point (°C)	97.00±0.00
Pour Point (°C)	-12.00±0.00
Calorific Value (MJ/kg^{-1})	24.00±0.10

Data are means of three replicates (n = 3) ± SEM using Graph Pad Prism, t-Test Source: Field data, 2022.

The pH of bio-oil from the feedstock was within the conventional bio-oil range of 2-3.8 because of organic acids, mostly acetic acid, and formic acid presents. The pH of bio-oil obtained from coconut shell agrees with pH of bio-oil produced from corn stover (3.0), big bluestem (3.4) and Praire cord grass (3.6) respectively as reported by Muthukumaparappan *et al.* (2011).

The bio-oil exhibits a low pH value and therefore is corrosive. Bio-oil generally contained substantial amount of organic acids, mostly acetic acid and formic acids, which give the bio-oil its low pH (2-3) Antonakou *et al*. (2006). Acids with water are the main reasons for the corrosiveness of pyrolysis bio-oils, especially at elevated temperatures (Antonakou *et al*. 2006).

Abdullah and Gerhauser (2008) described bio-oil as a highly dense liquid with a density around 1.2g/cm^{-3} which agrees with the values of density obtained for both samples as shown in Table 5. Shoujie *et al*. (2016) reported 1.13g/cm^3 for switchgrass derived bio-oil which compares well with the results obtained. Piyarat and Chaiyot (2007) reported 1.18g/cm^3 and 1.10g/cm^{3}as the density of palm shell bio-oil and cassava pulp residue, respectively and it was found that the density of the pyrolytic sample was higher than that of commercial diesel fuel, which corresponds to a higher energy content.

The moisture results obtained in this study are consistent with the results observed by Kang *et al.* (2013) which reported moisture content within the range of 27-38% for radiata pine fast pyrolysis in fluidized bed reactor with a hot vapour filter. It is also in agreement with many other results as reported by Oasmaa *et al*. (2009) and compare well to the palm shell bio-oil results reported by Abnisa *et al*. (2013a). Water content in fuel is not required since it reduces heating value, causes corrosion, and increases viscosity.

Ash is an impurity that will not burn, which reduces handling and burning capacity of any fuel. It increases handling cost and affects combustion efficiency, thereby causing clinkering and slagging. Excessive ash in fuel can cause fouling deposits in the combustion equipment. Ash is the incombustible material, which remains when fuel is burned. Ash is detrimental in combustion processes in which it lowers the calorific value of the fuel. Excessive amounts of ash can cause high wear in pumps and injectors and lead to deposits in combustion equipment Ogunsanwo and Adegoke (2011). The results obtained are higher than the result of rice husk-derived bio-oil of 0.03% as reported by Ige *et al.* (2020).

Acidity makes bio-oil very corrosive, and it is extremely severe at elevated temperatures, which imposes more requirements on construction materials of the vessels and the upgrading process before using bio-oil in transport fuels. The results of the acid value determination are shown in Table 5. The acid value of the bio-oil sample for coconut shell is 9.00mg KOH/g Duration of storage and drying of the biomass can increase the acid value. The acidity is attributed to phenols compounds such as those mentioned in Table 6 and the presence of carboxylic acid that is normally present in the bottom phase of bio-oil. Bio-oil acidity is a major cause of corrosion in materials such as carbon steel and aluminum.

The viscosity of bio-oil values reported in this study is lower than the viscosity of *Gmelina arborea* (14.00cSt) reported by Adegoke *et al.* (2020) as shown in Table 5. Viscosity is a property that represents the flow characteristics of the fuel. High viscosity in fuel leads to several problems such as incomplete combustion, formation of deposits at the tip of injection nozzles and contamination of lubricating oils (Antonakou *et al.* 2006). The increase in viscosity is caused by heavier tar compounds found in biomass.

The flash point value in this report compared well with 68°C obtained for the *Swietenia macrophylla* bio-oil as reported by Chukwuneke *et al.* (2019). Flash point is a measure of the liquid temperature necessary for the vapors above a pool of the fuel to ignite by passing a flame through the vapors. This is also a measure of the volatility of the oil, as well as its ease of ignition. The higher this number, the safer the oil for handling, because of the risk of accidental vapor ignition.

Pour point is a criterion used for low temperature performance of a fuel. The pour point value recorded in this study would not cause any trouble in most of the tropical regions and colder regions. The result of the pour point obtained in this study is within the ASTM range of (-15 – (-10°C)) and compares well with -14°C and -17°C reported for palm shell and cassava pulp respectively (Shojie *et al*. 2016).

The result of the heating value recorded in this study (24.00MJ-kg^{-1}) which was similar to the ASTM specification (43MJ-kg^{-1}) and the result is well compared to the values obtained for other bio-oils as reported by Okoroigwe *et al.* (2015), Hossain *et al*. (2014) and Oyebanji *et al*. (2017) respectively. Above all, pyrolysis oil is close to ASTM standard for biodiesel (35-40MJ-kg^{-1}) and fossil diesel (45MJ-kg^{-1}) makes it fit to be used as fuel.

Table 6

GC-MS table of the compounds present in Coconut Shell Bio-oil

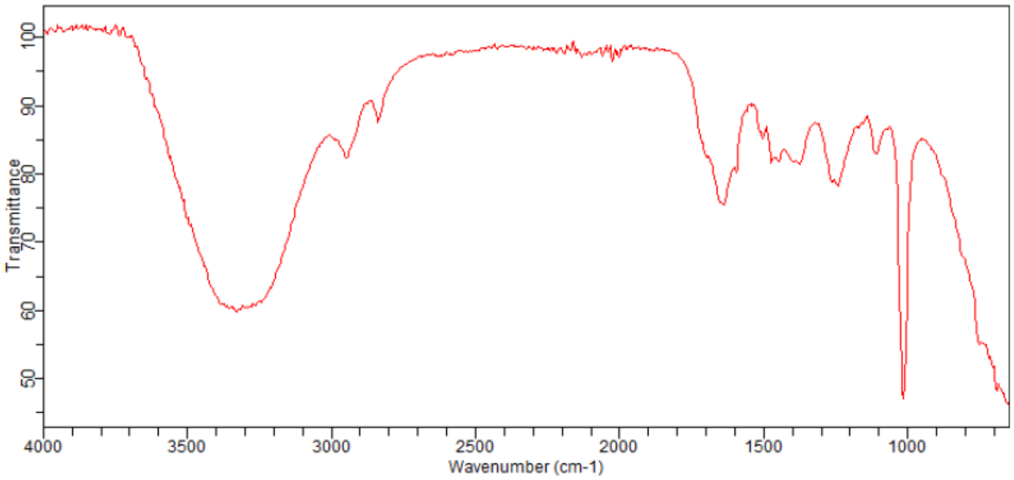
S/N	Name of compounds	Compound Formula	Retention Time	% Composition
1.	P-cresol	C_7H_8O	7.505	4.779
2.	Cyclohexene	C_6H_{10}	9.076	1.184
3.	Phenol	C_6H_6O	10.318	24.084
4.	o-Methoxy	$C_{10}H_{14}O_2$	9.480	3.256
5.	Benzofuran	C_8H_6O	10.745	1.163
6.	Eugenol	$C_{10}H_{12}O_2$	11.149	2.282
7.	Benzene	C_6H_6	12.016	1.872
8.	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	16.087	2.024
9.	Cis-13-octadecanoic acid	$C_{18}H_{34}O_2$	16.746	2.443
10.	Pyrene	$C_{16}H_{10}$	17.179	1.326
11.	Cis-vaccenic acid	$C_{18}H_{34}O_2$	17.369	3.848
12.	Tetradecanamide	$C_{14}H_{29}NO$	17.670	1.221
13.	Ethyl-9,12-Hexadecadienoate	$C_{18}H_{32}O_2$	17.877	1.211
14.	3, 5- dimethylthiophenol	$C_8H_{10}S$	18.813	3.670
15.	Docosanoic acid	$C_{22}H_{44}O_2$	19.702	1.928
16.	Tetracosanoic acid	$C_{24}H_{48}O_2$	20.956	1.880
17.	1-propyl-14-methyl hexadecanoate	$C_{18}H_{36}O_2$	21.256	1.701
18.	Cinnamaldehyde	$C_9H_{36}O$	22.371	1.867
19.	Longifolenaaldehyde	$C_{15}H_{24}O$	22.648	1.050
20.	Stigmasta -3, 5- diene	$C_{29}H_{48}$	23.168	1.606
21.	1-octadecene	$C_{18}H_{36}$	23.57	0.42
22.	Triacontanoic acid, methyl ester	$C_{31}H_{62}O_2$	24.26	0.33
23.	Z-8-methyl-9-tetradecen-1-ol Acetate	$C_{17}H_{32}O_2$	25.23	0.70
24.	Stigmast-4-en-3-one	$C_{29}H_{48}O$	25.95	0.55
25.	5-methyl-6-phenyl Tetrahydro-1,3-oxazine -2-thione	$C_{11}H_{13}NOS$	28.92	0.15

Source: Field data, 2022

The GC-MS analysis was carried out in order to find out the compounds present in both types of optimized bio-oil samples. Both groundnut shell and rice husk bio-oil are complex mixtures and contain different classes of hydrocarbons and other compounds which are shown inTable 6.

The GC-MS result indicates the presence of different compounds which include fatty acids, aldehyde compound, nitrile, esters and many others. The most abundant compound phenol (24.084%) accounted for the total bio-oil produced. Phenol is proven to be an effective anti-bacterial, anti-fungal and anti-viral agent. The fatty acids, including cis-vaccenicacid, tetracosanoic acid, docosanoic acid etc., and nitrile compounds are assumed to be derived from protein degradation (Antonakou *et al.* 2006).

The chemical compounds identified in the biomass are consistent with the findings of various authors in their research work (Kanaujia *et al.* 2016, Kongkasawan *et al*. 2016). The results confimed that the bio-based product (bio-oil) will provide an alternative to many petroleum based chemicals, which are mostly toxic and non-degradable in the environment (Lasode *et al*. 2014). The results also confirmed that the pyrolysis of cellulosic biomass gives water soluble oxygenated compounds. This work shows that some organic acids which can lead to high corrosivessness can be decreased by pre-treatment of the biomass before pyrolysis.



Source: Field data, 2022.

Fig. 6.
FTIR Spectrum of Coconut Shell Bio-oil.

Table 7

Fourier transform infrared spectroscopy (FTIR) peaks for Coconut shell bio-oil

S/N	Compound Class	Group	Absorption (cm^{-1})	Appearance
1.	Alcohol,	O-H Stretch	3331	Strong, Broad
2.	Alkane	C-H Stretch	2948	Medium
3.	Aromatic compound	C-H Bend	2840	Weak
4.	Alkene	C=C Stretch	1640	Medium
5.	Aldehyde	C-H Bend	1380	Medium
6.	Alkyl ether	C-H Stretch	1246	Strong

Source: Field data, 2022.

Bio-oil is composed of extremely complicated organic compounds. Although different bio-oils from different raw materials express some common chemical characteristics, detailed chemical composition will vary tremendously with the different raw materials, pre-treatment methods, pyrolysis condition and the collection method of products (Liu *et al.* 2017). Fig. 6 shows the infrared spectra of coconut shell bio-oil. Fig. 6 revealed that there was an apparent stretching vibration band at 3331cm^{-1}. This is evidence of the presence of alcohols and phenols in the coconut shell bio-oil as shown in Table 7. Simultaneously, C-H stretching vibration band 2948cm^{-1} could also be noted as an alkane compound.

The bending vibration at 2840cm^{-1} indicated aromatic compounds, a medium C=C stretching vibration was observed at 1640cm^{-1} while a medium C-H bending vibration observed at 1380cm^{-1} confirms the presence of aldehyde compounds in the bio-oil. In a typical FT-IR spectrum, the region from 1500 to 400cm^{-1} is termed as fingerprint region where the bands are densely occupied (Gilbert 2017).

CONCLUSION

In this study, the physio-chemical properties of coconut shells were analyzed and with the results obtained it can be concluded that coconut shells can be a good raw material to produce bio-oil. Bio-oil from coconut shell was produced under optimal conditions in a fabricated fixed bed reactor and the bio-oil was characterized. At optimum variable conditions, bio-oil yield of 44.25wt percent was obtained, which compares favorably with previous literature. The results of the FT-IR analysis confirm the presence of functional groups O-H, C-H, and C=O in the bio-oil sample. The result of the GC-MS analysis revealed the presence of major compounds such as phenol, p-cresol, and cis vaccenic acid. Bio-oil derived from coconut shells should be treated and upgraded before being used as an alternative fuel. When using bio-oil in internal combustion engines, the corrosion problem should be considered due to the high special additives' acid values.

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