



OPTIMIZATION OF BIOFUEL PRODUCTION FROM PYROLYSIS OF TERMINALIA CATAPPA PELLETS IN A FIXED BED REACTOR

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ABSTRACT

Pyrolysis stands out as an effective thermochemical pathway for transforming biomass to biofuels. This study focused on the optimization of bio oil and bio char production through pyrolysis of Terminalia Catappa Pellets (TCP) using a fixed bed reactor. Box-Behnken Design (BBD) under Response Surface Methodology of Design Expert software version 13.0 was employed for the modelling and optimization of bio char and bio-oil yield at a specified range of temperature (450 – 600 oC), holding time of (15 – 60 mins) and particle size (0.5 – 2.0 mm) within an inert atmosphere fixed bed reactor. The chemical properties of bio-oil were investigated using GC-MS. The maximum bio-oil yield (52.50 %) and bio char (22.80 %) were observed at a temperature of 525oC, holding time (15 mins) and 1.25 mm particle size. The GC-MS showed that bio oil contained acetic acid, l-hydroxyl-2-proanone, and acetic acid-methylester with the highest peak areas of oxygenated compounds. Further processing of these chemicals could make it suitable for industrial applications. The mathematical models for the bio-oil and bio-char through pyrolysis using the BBD indicated a strong fit with coefficient of determination (R²) values of 0.97 and 0.98 respectively. The prediction accuracy suggests that BBD can be applied for prediction of biofuel through pyrolysis of biomass pellets.

Keywords: Pyrolysis; Bio-oil; Terminalia Catappa Pellets; Fixed bed reactor; Box-Behnken Design.

1.0 INTRODUCTION

Regardless of the country concerned, energy is a major factor in enhancing economic development. In a third-world nation like Nigeria, lack of reliable electricity supply continues to be the principal barrier to general growth. Nigeria continues to be the sixth-biggest oil producer in the world and the largest producer of crude oil in Africa (Anil et al., 2017). Petroleum is the country's primary source of energy, however, due to the lack of efficient petrochemical and refinery sectors, the majority of petrochemicals and petroleum refining byproducts, including lubricants, grease, gasoline, hydraulic fluid, diesel, and even oil used in the transformers are imported. Furthermore, the necessity for alternate energy sources for industrial applications has been fueled by the considerable pollution connected to petroleum-based products because of their non-biodegradability (Asif et al., 2022). Biomass has been seen as a reliable and sustainable energy source that may be used to create a variety of chemicals and materials (Kareem et al., 2018; Oladosu et al., 2021).

Low sulfate and nitrogen content, as well as the absence of net CO₂ emissions into the atmosphere, make biomass preferable to traditional fossil fuels (Ayman et al., 2019). A variety of elements, including forest leftovers, energy crops, organic wastes, agricultural residues, and others, are included in the term "biomass resources." Agricultural biomass leftovers have a high energy content and are made up of cellulose, hemicellulose, and lignin (Ayman et al., 2019 ; Chinedu et al.,

2019). Solar energy, hydropower, wind turbines, biomass, and agricultural residues are all examples of renewable energy (Chinedu et al., 2022).

According to (Muhammad et al., 2013), vegetable oil must now be used as a significant and trustworthy substitute when compared to petroleum. Vegetable oils are renewable, biodegradable, and environmentally beneficial. The need for nut and seed, particularly those with non-food competitors and oil content has recently increased for the manufacturing of bio-oils. In order to fulfill the rising demand from home and industrial sectors, the vegetable oil industry must be developed (Mohan et al., 2006). The National Cereals Research Institute (NCRI), National Institute for Palm Oil Research (NIPR), and Forestry Research Institute of (FRI), all of which are located in Nigeria, and all have developed, improved and high oil yielding seeds and nuts. Due to their high oil outputs, many plant seeds and nuts constitute a significant source of oil for industrial uses in Nigeria, among these seeds/nuts are Sesamum indicum L.(sesame), Jatropha curcas, Arachis hypoogaea Linn (groundnut), Elaeisguineensis (palm) oil, and Cocosnucifera (coconut), though nearly all of them are food competitors. This present study, take into account terminalia catappa biomass because of its non-food competing character, and comparatively high oil output and quality (Goutam et al., 2019). Potential applications of raw biomass are restricted because of certain issues such as poor grindability, low energy density, hygroscopic nature, and oxygen content, low bulk/particle

density and high moisture content, among others, These can be solved by biomass densification (pelletization) in combination with pyrolysis which has received great attention. This process of pelletization greatly lowers the cost of handling, transportation, and storage while increasing the density of biomass.

According to several studies (Ndukwu et al., 2021; Kumar et al., 2019), pyrolysis is a popular thermochemical technique for efficiently turning biomass into liquid, biochar, and gas at temperatures as low as 300 –600 oC. Pyrolysis is the fast heating of biomass to temperatures of 300°C to 650°C or even higher, which results in the breakdown of biomass into non-condensable gases (primarily H₂, CO, CO₂ and CH₄), liquids (tar and water), and solid (char) products in an inert environment. The combination of pelletization and pyrolysis is a highly efficient method for enhancing pellets properties including the carbon content, energy density, resistance to moisture absorption, ease of grinding and inhibiting bacterial growth

The modeling, optimization and potential application of bio-oil yields of terminalia catappa pellets are crucial due to the comparatively high oil output of terminalia catappa. In doing so, the intended final product will have the highest possible yield. In this study, Box-Behnken design under Response Surface Methodology was required for the pyrolysis process in order to provide the best of the bio-oil yield. According to Wang et al. (2020), RSM is an efficient mathematical and statistical tool for optimizing process variables.

RSM have been deployed for the prediction and optimization of bio-oil, bio char and non condensable gases of pyrolyzed biomass. Among them municipal solid waste (Chen et al., 2021) are non-oil jatropha caucus (Kethobile et al., 2020), sugarcane bagasse (Ahmad et al., 2018) palm kernel shell (Kareem et al., 2018; Ozonoh et al., 2020), Acacia nilotica (Singh et al., 2020) among others. Though the list is not exhaustive, but none of the others have reported optimization

or prediction of bio oil yield during pyrolysis of terminalia catappa pellets using RSM. This study, therefore, reports process modeling, prediction, and optimization of TCP pyrolysis process for maximum value of bio-oil yield which is a requirement for commercialization.

2.0 MATERIALS AND METHOD

2.1 Collection and Preparation of Samples

The terminalia catappa samples were collected from Okene, Kogi State, Nigeria. Prior to the pelletization and pyrolysis process, the outer seed coatings of the samples were removed carefully and the kernels were separated and subjected to a thoroughly cleaning process. Afterwards, they were sun dried, milled and sieved to achieve different particle sizes ranges (0.5-2 mm). The pelletization process was performed using a flat die pellet machine in order to reduce the void spaces between particles in the reactor bed, promoting better heat transfer and more efficient pyrolysis reactions. The different particle size of terminalia catappa biomass was compressed into the shape of a pellet. The material was conditioned and subjected to thermal treatment within the specified design of the pellet mill. Subsequently, the feed was pushed through a perforated hole and then emerged as a pelletfeed. After pelletization process, the pellets were left to cool down at room temperature and were kept in a closed plastic bags prior to pyrolysis test.



Plate 1: Image of terminalia catappa fruit.



Plate 2: Images of terminalia catappa kernel grinded and sieved to different sizes (0.5mm, 1mm, and 2mm respectively)

2.2. Design of the Experiment using Response Surface Methodology (RSM)

Box-Behnken Design under the Response Surface Methodology (RSM) was employed for the design and optimization of the process parameters. The experimental design involved choosing the minimal set of design parameters and conducting a specific number of experimental trial to develop the most reliable regression models. In this study, the designed experiment were within the ranges of the process factor such as temperature, holding time and particle size as shown in (Table 1). The nitrogen gas flow rate (75 mL/min) was kept constant (Oladosu et al., 2021)

Table 1: Minimum and Maximum values of Experimental Parameters.

	Temp (°C)	Time (mins)	Particle size (mm)
Minimum value	450	15	0.5
Maximum value	600	60	2

2.3. Experimental Set up and Operation

The pyrolysis apparatus consists of a vertical fixed-bed reactor made of stainless steel (5 cm) wide and 65 cm long, with a distribution plate inside the heating element that is 8 cm from the bottom and has a diameter of 1.0 mm (see Figure 1). The TCP samples were charged into the reactor in preparation for thermal decompositions of pellet samples in an inert gas environment based on the experimental design for a specific range of temperature, holding time and particle sizes. To account for convective heat loss, the reactor temperature was

set at 35 degree celcius above the targeted temperatures. Consequently, the samples were gradually heated while being exposed to nitrogen gas. The condenser unit was immersed in an ice salt bath, was connected to the reactor to facilitate flue gases condensation, the gas sample was employed to collect non condensable gases. After the prescribed holding time the char was removed from the reactor and allow to cool and then measured. This procedures was followed for all biomass samples at different heating times and pyrolysis temperatures based on the experimental design. After each experiment, the product yields were evaluated according to Equations 1-3.

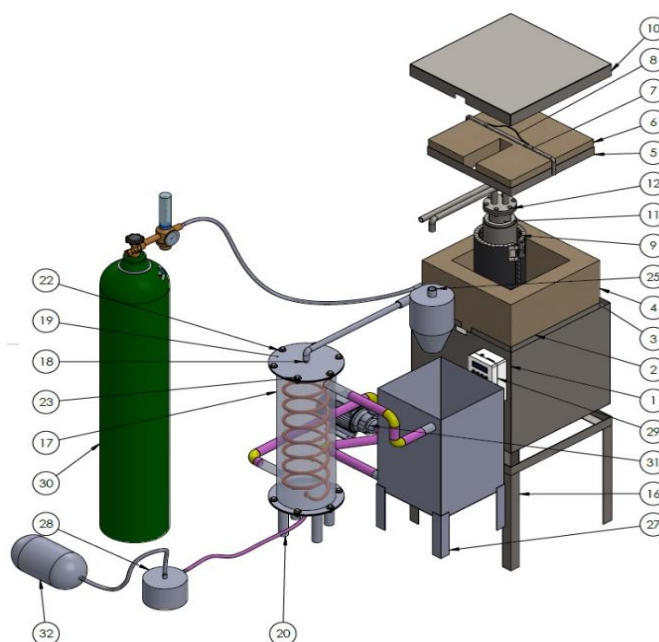


Fig. 1. Fixed bed pyrolytic unit

Table 2: Description of parts of the pyrolytic unit.

Item	Part list	Qty	Item	Part list	Qty
1	Combustion chamber enclosure	1	17	Condenser barrel	1
2	Combustion chamber enclosure	1	18	Condenser coil	1
3	Inter enclosure cover	1	19	Top condenser lid	1
4	Refractory bricks	Lot	20	Bottom condenser welded	1
5	Top refractory bricks frame	-	21	Condenser gasket	1
6	Combustion chamber top refractory	1	22	B 18.22m plain washer narrow	12

7	Top refractory frame hang	1	23	B 18. 2.3.2 m hex-screw M10 x 1.5 x 25-25 CN	12
8	Top refractory handle	1	24	B 18. 22.4 m Hex flange nut M 10 x1.5 with 15 WAF N	12
9	Heating element	1	25	Cyclone	1
10	Combustion chamber lid	1	26	Biomass piping	1
11	Reactor	1	27	Biomass water tank	1
12	Reactor lid	1	28	Bio oil collector	1
13	Reactor gasket	1	29	Custom control box	1
14	B 18.6.7m-m8x1.25x30 indented	1	30	Nitrogen gas cylinder	1
15	B 18.2.24M Hex flange nut M8x 1.25N	6	31	0.5hp water pump	1
16	Combustion chamber stand	1	32	Gas bag	1

$$\% \text{ Char yield} = \frac{\text{Mass of the char obtained after pyrolysis}}{\text{Mass of the dried raw biomass}} \times 100\% \quad (1)$$

$$\% \text{ Bio-oil yield} = \frac{\text{Mass of the liquid obtained after pyrolysis}}{\text{Mass of the dried raw biomass}} \times 100\% \quad (2)$$

$$\% \text{ Gas yield} = 100 - (\text{Bio-oil yield \%} + \text{Char yield \%}) \quad (3)$$

2.4 Gas Chromatography Analysis of Bio-Oil

The chemical components were separated with Agilent 6890 gas chromatograph equipped with an on-column automatic injector, flame ionization detector, and HP 88 capillary column (100 m x 0.25 µm film thickness) (made in the USA). The temperature of the gas chromatographer column was initially set at 160 °C for 2 mins, increased to 180 °C at 6 °C/min, maintained for 2 mins at 180 °C, then further increased to 230 °C at 4 °C/ min, and finally maintained for 10 min at 230 °C. The temperature of 230 and 250 oC was maintained for the injector and detector while the split ratio was 50:1.

3.0 RESULTS AND DISCUSSION

3.1. Proximate and Elemental Composition of Terminalia Catappa Pellets

The proximate analysis of the TCP showed the attendance of volatile matter (73.44%), fixed carbon (16.95%), moisture content (5.48%), and ash content (4.25%) (Table 3). A higher proportion of volatile matter enhances the attractiveness of biomass as a feedstock for pyrolysis (Jie et al., 2021). Based on elemental composition, the feedstock contained carbon (43.67%), oxygen (39.07%), hydrogen (17.23%), nitrogen (0.56), and sulphur (0.02%). This aligns with findings from the previously conducted study (Kenechi et al., 2022). This brings to bear the vital elements that influence energy value and emission

Table 3. Proximate and elemental composition of TCP

Analysis	Component	Composition (wt. %)
Proximate	Moisture	5.48
	Ash	4.25
	Fixed Carbon	16.95
	Volatile Matter	73.44
Ultimate	Carbon	43.67
	Oxygen	39.07
	Hydrogen	17.23
	Nitrogen	0.56
	Sulphur	0.02

3.2. Statistical Assessment of the Model Predictions in Comparison to Experimental Data

The experimental and corresponding predicted values for each experimental run are presented in Table 4. The optimal process conditions to produce pyrolyzed biomass were determined from the experimental runs (Table 4). Thus, the optimal process conditions for the maximum bio-oil (52.40 %)

at the temperature of 525 °C, the residence time of 38 mins and particle size of 1.25 mm. Analysis of variance (ANOVA) was used to statistically investigate the responses, biochar and bio-oil yields. These analyses were carried out to assess the fitness of the models generated using coefficients of determination (R^2), and the mean square errors (MSE). Table 5 represents ANOVA obtained for the biochar and oil yields of pyrolyzed TCP, respectively. The analyses of the P and F values is crucial before approving any model; when the F-value is large, the model's dependability is better, whereas with a lower P-value, the model's significance is higher (Mudasir et al., 2021). Regression analysis was used to determine the correlation between the independent parameters (temperature, residence time, and particle size) and the dependent variables (bio-oil and bio-char). The derived model for predicting the bio-oil and bio-char as a function of temperature, residence time, and particle size as obtained from the Design-Expert version 13.0 are provided in Equations 1 and 2, respectively. Equation 1 indicates the presence of linear, square and crossed terms for the variable investigated in bio-oil and Equation 2 indicates the presence of linear and square terms for the variable investigated in bio-char. The relationship between the experimental and forecasted values for bio-oil and bio-char are presented in Figures 2 (a) and (b) correspondingly. There was good agreement and consistency

between the data sets of the experimental and predicted values. This affirmed the accuracy of the reported model and its usefulness for predicting the bio-oil and bio-char.

$$\text{Bio char yield} = +22.80 - 0.9087A - 3.71B - 3.71B - 3.07C - 0.5725AB + 0.245AC + 2.44BC + 9.24A^2 + 4.39B^2 - 6.92C^2 \quad (5)$$

$$\text{Bio oil yield} = +52.405 - 0.8825A - 0.2375B + 1.61C + 0.5500AB + 0.3500AC - 1.70BC - 10.43A^2 - 8.34B^2 - 7.51C^2 \quad (6)$$

where; A = temperature, B = holding time, C = particle size. At a 95% confidence level (Table 5) the terms in the equations are said to be significant when the p-value is less than 0.5. Accordingly, B, C, BC, A^2 , B^2 , C^2 are significant for bio-char yield with strong interaction, for bio-oil yield, the most significant terms are A^2 , B^2 , C^2 . The model F value of 31.29 and 25.33 for bio-char and bio-oil respectively suggest that the model is statistically significant. Furthermore, standard deviation (1.73 and 2.22 for bio-char and bio-oil yield, respectively), coefficient of determination R^2 (0.98 and 0.97), R^2 Adj (0.94 and 0.93), and other parameters backed the accuracy and adequacy of the models.

Table 4. Experimental runs and Responses Based on Box-Behnken Design

Run	Temp (deg C)	Time (min)	P.size (mm)	Char yield (%)			Bio –oil yield (%)		
				Actual	Predicted	Residual	Actual	Predicted	Residual
1	525	60	0.50	16.85	17.19	-0.3412	36.50	36.40	0.1000
2	600	38	2.00	23.14	21.39	1.7500	35.62	35.54	0.0800
3	525	60	2.00	14.28	15.94	-1.6600	38.85	36.23	2.6300
4	525	38	1.25	24.50	22.80	0.0000	49.30	52.40	0.0000
5	525	38	1.25	22.80	22.80	0.0000	52.40	52.40	0.0000
6	450	15	1.25	40.57	40.47	0.0950	38.00	35.29	2.7100
7	600	15	1.25	37.71	39.80	-2.0900	32.45	32.43	0.0200
8	525	15	2.00	18.80	18.46	0.3413	40.00	40.10	-0.1000
9	525	38	1.25	21.60	22.80	0.0000	52.31	52.40	0.0000
10	450	38	0.50	27.60	29.35	-1.7500	34.00	34.08	-0.0800
11	600	60	1.25	31.15	31.24	-0.0950	30.35	33.05	-2.7000
12	525	38	1.25	21.90	22.80	0.0000	51.74	52.40	0.0000
13	525	15	0.50	31.15	29.49	1.6600	30.85	33.48	-2.6300
14	525	38	1.25	22.80	22.80	0.0000	50.40	52.40	0.0000
15	450	60	1.25	36.30	34.21	2.0900	33.70	33.72	-0.0200

16	600	38	0.50	27.48	27.04	0.4362	34.22	31.61	2.6100
17	450	38	2.00	27.28	22.72	-0.4362	34.00	36.60	-2.6000

Table 5. ANOVA for the char and oil yields

Source	Sum of Squares	Df	Mean Square	F-value	P-value	
Bio-char						
Model	838.46	9	93.16	31.29	< 0.0001	Significant
A-temperature	6.53	1	6.53	2.19	0.1820	
B-time	109.96	1	109.96	36.94	0.0005	
C-PS	76.85	1	76.85	25.81	0.0014	
AB	1.21	1	1.21	0.4073	0.5436	
AC	0.2401	1	0.2401	0.0806	0.7846	
BC	24.19	1	24.19	8.13	0.0247	
A ²	359.68	1	359.68	120.81	< 0.0001	
B ²	78.02	1	78.02	26.21	0.0014	
C ²	201.48	1	201.48	67.68	< 0.0001	
Residual	20.84	7	2.98			
Lack of Fit	20.84	3	6.95			
Pure Error	0.0000	4	0.0000			

R² = 0.99, R²_{Adj} = 0.9446, Standard deviation = 1.73, mean = 25.96, coeff. of variation (%) = 2.78,

Bio-oil yield

Model	1125.34	9	125.04	25.33	0.0002	Significant
A-temperature	4.18	1	4.18	0.8461	0.3882	
B-time	0.0365	1	0.0365	0.0074	0.9339	
C-PS	21.29	1	21.29	4.31	0.0764	
AB	3.36	1	3.36	0.6798	0.4369	
AC	0.4900	1	0.4900	0.0993	0.7619	
BC	11.94	1	11.94	2.42	0.1638	
A ²	443.45	1	443.45	89.83	< 0.0001	
B ²	281.25	1	281.25	56.97	0.0001	
C ²	248.19	1	248.19	50.27	0.0002	
Residual	34.56	7	4.94			
Lack of Fit	34.56	3	11.52			

Pure Error 0.0000 4 0.0000

$R^2 = 0.970$, $R^2_{Adj} = 0.932$, Standard deviation = 2.2, mean = 40.11, coeff. of variation (%) = 5.54

After successfully developing precise model, we then used them to make prediction and subsequently compare the predictions with experimental data. As a result, the majority of the data are almost linear with coefficient of determination (R^2)

of approximately 1, indicating high agreement between the model response and experimental data. These models can always be used to predict the yields of biochar and bio-oil.

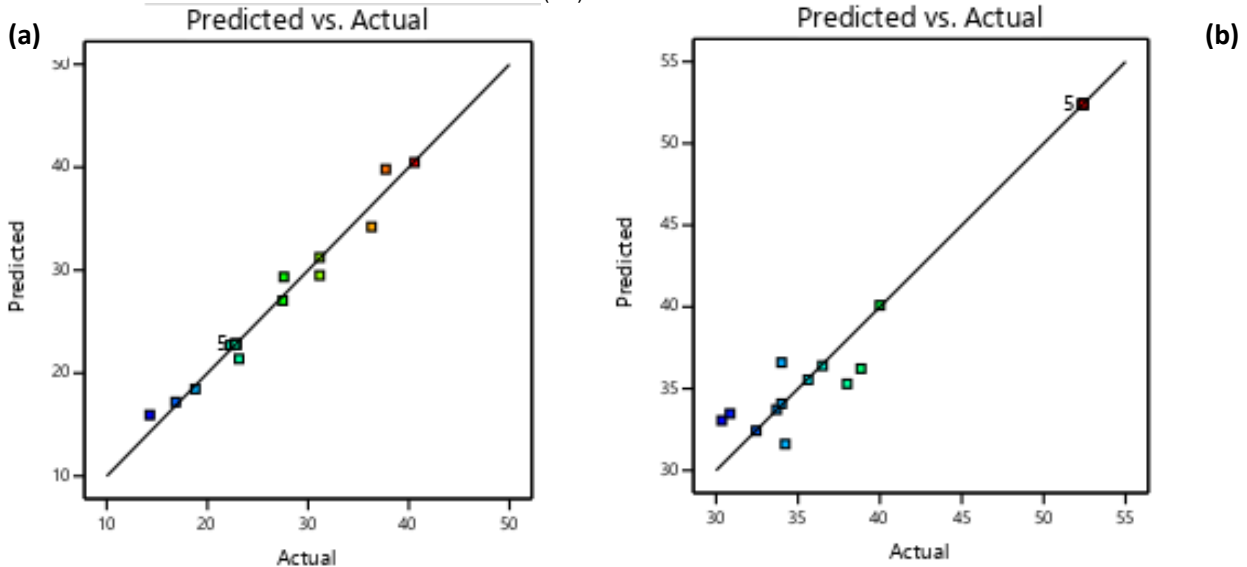
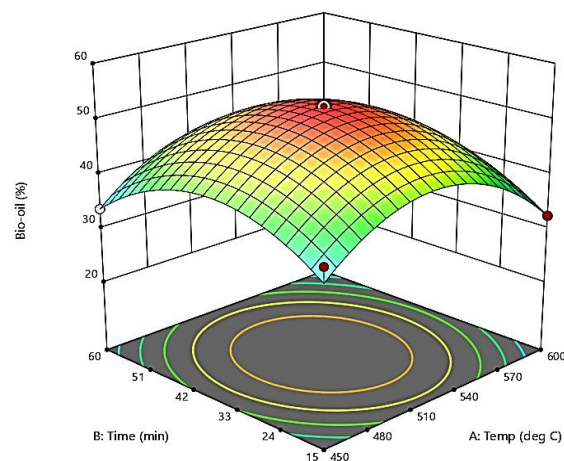


Fig 2: Predictions and experimental data of (a) bio char and (b) bio oil yield by TCP pyrolysis

3.3 Influence of Process parameters on bio-oil and bio char yield

The influences of temperature and time, time and particle size, on bio oil yield and temperature and time on bio char yield were critically examined using 3D response surface plots (Fig. 3 a-c). The bio-oil increased with temperature up to 525 °C and for an increase in residence time up till 38 min (Fig. 3a). At 525 °C, 52.4 % of bio oil yield was obtained compared to 33.70 % at 450 °C. Likewise, Bio oil yield increased by 41.1 % when the holding time was increased from 15 to 38 min keeping other variables constant. Conversely, biochar decreases from 40.57 % to 22.80 % for the same range of temperature and time (Fig. 3c). It was also observed that size of the particles at 1.25 mm raise bio-oil and lower biochar at increase pyrolysis temperature and holding time (Fig 3b). In this case, the maximum bio oil yield (52.4 %) was obtained at a temperature of 525 °C, holding time of 38 mins and particle size of 1.25mm. while the maximum bio char of 40.57 % was obtained when the temperature was 450 °C at the same particle size but holding time of 15 mins. This finding is in line with the work of (Nahieh et al., 2021) that higher temperature promotes the decomposition of biomass and more gaseous and liquid products thereby favouring the formation of bio oil. However,

the yield of biochar decreases as the pyrolysis temperature increase (Ogunkanmi et al., 2018).



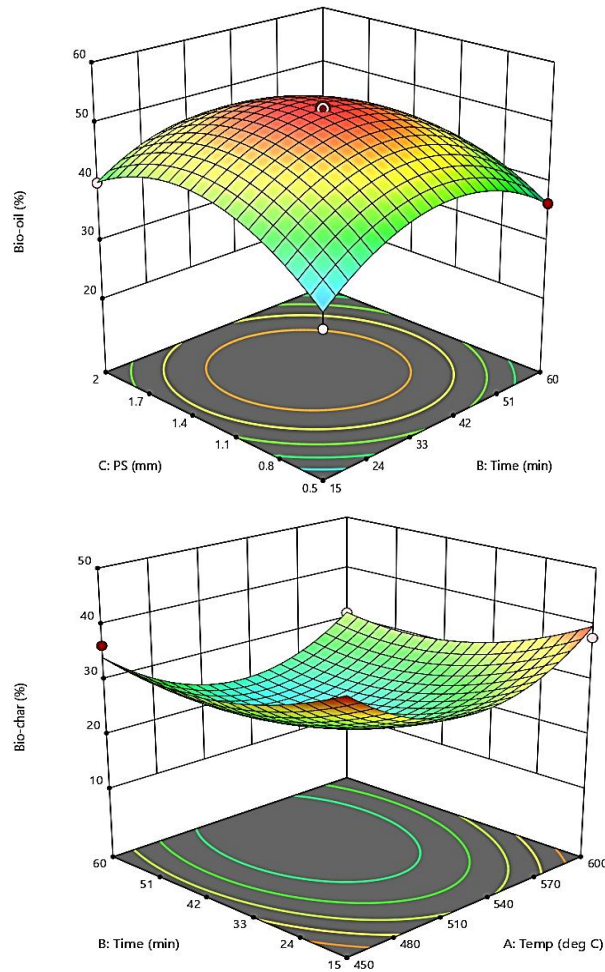


Fig. (3a-c): The 3D response surface plot showing the effect of temperature and time, time and particle size on bio oil yield and temperature and time bio char yield

3.4 Analyzing bio-oil using GC-MS

The GC-MS analysis identified the chemical components present in the pyrolytic liquid (Fig. 4 and Table 6). Table 6 lists the presence and retention times of significant volatile chemical components in terminalia catappa bio-oil. The compound name and peak area percent are also included. Bio-oil's GC-MS indicates the presence of many chemical components. The main class of oxygenated chemicals found in bio-oil are aldehydes, ketones, carboxylic acids, and esters. After the cellulose and hemicellulose part of biomass has broken down, oxygenated molecules such 1-hydroxyl 2-proanone, 1-hydroxyl 2-butanone, acetic acid-methyl ester, etc. are created (Yorgan and Tildiz, 2015). According to the results, acetic acid, 1-hydroxyl-2-proanone, and acetic acid-methylester had the highest peak areas of oxygenated compounds, with respective peak areas of 27.38%, 16.40%, and 3.65%. Additionally, it suggests that phenol evolves more slowly at higher temperatures.

Table 6: Major chemical compounds in the optimized bio-oil yield sample classified by GC-MS.

S/No.	RT (mins)	Compound Name	Area %
1.	8.20	2-amino 1,3-propanediol	1.50
2.	9.40	Acetic acid	27.38
3.	10.95	1-hydroxyl 2-proanone	16.40
4.	15.60	1-hydroxyl 2-butanone	1.85
5.	15.85	Acetic acid-methylester	3.65
6.	18.05	Butanediol	2.55
7.	18.80	2-cyclopentane-1-one	1.70
8.	18.60	Furfural	2.30
9.	20.85	2,2,4-trimethyl-1,3-dioxolane	1.50
10.	21.65	1,2-propanone	2.65
11.	22.05	2-butanone	1.20
12.	26.95	2,3-dimethyl-cyclopentane	1.25
13.	27.80	2-furanone	1.15
14.	29.70	3-methyl 1,2-cyclopentanedione	3.20
15.	31.50	Phenol	3.05
16.	35.70	4-methyl-phenol	1.30

17.	39.70	4-ethyl-phenol	2.15
18.	43.62	2,3-dihydro-benzofura	3.65
19.	59.95	Glucosandi-one	2.30

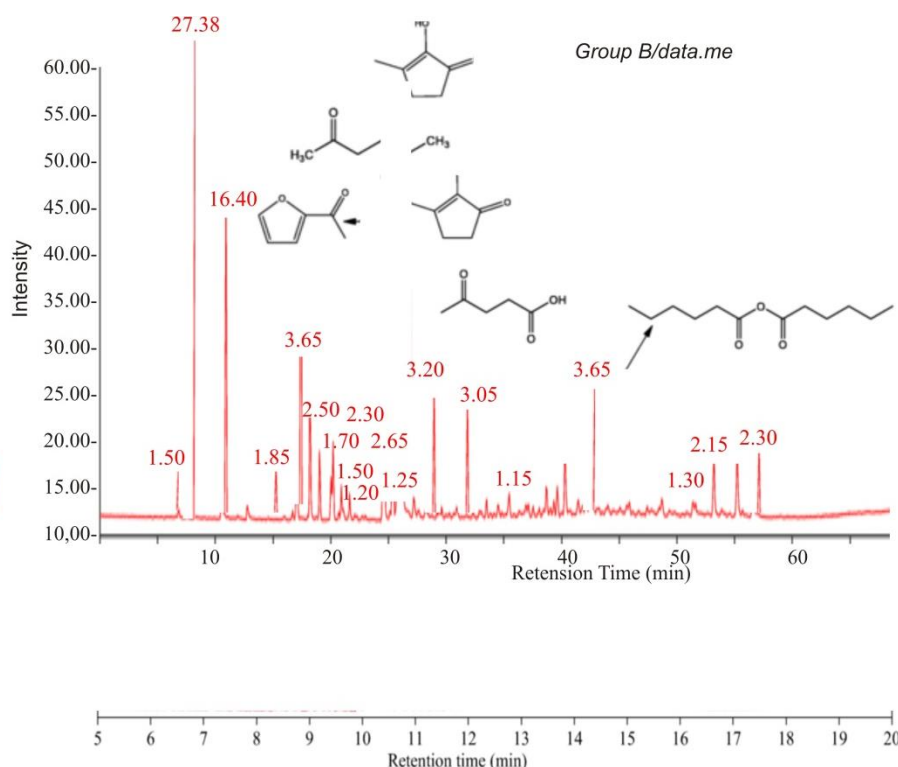


Fig.4 Chromatograph of GC-MS Analysis of the optimized bio-oil yield

4.0 CONCLUSION

Pyrolysis of Terminalia catappa pellets was successfully conducted in a fixed reactor while the process parameters were modelled using Response Surface Methodology. The bio-oil and bio-char were optimized based on the process factors such as temperature, holding time and particle size. The optimum temperature was found at 525 °C for bio-oil and 450 °C for bio-char. At the particle size of 1.25 mm, the maximum bio-oil (52.40 %) was obtained at the temperature of 525 °C, holding time of 38 mins and particle size of 1.25 mm with biochar of (22.8 %). At same particle size of 1.25 mm, the maximum bio-char (40.57 %) was obtained at the temperature of 450 °C, and holding time of 15 mins with bio-oil yield of (38 %). The quadratic terms were found to be significant for the RSM models based on the MSE and R^2 values. The prediction accuracies indicates that RSM can be deployed for the accurate prediction of bio-oil and bio char in the pyrolysis of TCP pellets

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