

Optimization of pyrolysis conditions for production of rice husk-based bio-oil as an energy carrier

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ABSTRACT

Bio-oil is an eco-friendly energy source with potential to substitute fossil-derived fuels. This study optimized pyrolysis conditions for production of bio-oil from rice husks. Response surface methodology based on central composite design was employed to maximize bio-oil yield and high heating value (HHV) while minimizing water and ash contents. The pyrolysis process conditions were; temperature (400–650 °C), heating rate (6000–9750 °C/h), and holding time (600–1800 s). Analysis of variance revealed that the linear model best fits the responses of bio-oil yield and water content. On the other hand, the quadratic model best fits the responses of HHV and ash content. Pyrolysis temperature had the greatest influence on each of the studied responses, followed by holding time and lastly heating rate. Optimum pyrolysis conditions were found to be; temperature (650 °C), heating rate (9750 °C/h), and holding time (1800 s), leading to bio-oil yield, HHV, water and ash contents of 38.13%, 23.40 MJ/kg, 18.27%db and 0.16%db, respectively. These results fall in the range of standard quality values for bio-oil in published literature where >15 MJ/kg, 20–30%, 0.15–0.25% are the recommended ranges for HHV, water and ash contents, respectively. Results from the FTIR spectroscopy revealed that phenolic compounds contributed the most to bio-oil composition. Phenolic compounds positively influenced the quality of bio-oil due to their high calorific values. Gas chromatograph and mass spectrometry results showed peaks continuing to spill up to the maximum retention time indicating good thermal stability and bio-oil quality.

1. Introduction

In the past few decades, bio-oil has attracted immense research attention as a potential eco-friendly alternative to fossil fuels. Bio-oil has been commonly derived from waste biomass such as woods, agricultural residues, aquatic plants, and organic wastes [1]. These wastes are vastly generated in developing countries that hugely depend on agriculture. Africa aims at increasing food production such as rice by almost double the current production levels come 2030 [2] to enhance food security and household incomes. This projected increase in agricultural production is likely to result in wastes far in excess of any immediate local needs, for example, ricehusks are estimated to constitute about 20% of the total paddy weight [3] and are often unsustainably disposed off through open dumping or burning [4]. This implies that a great amount of rice husks is available as a potential bio-oil production precursor. Various uses of rice husks have existed for a long time. For example, rice husks (RH) are incorporated into soil to improve fertility after being

charred [5], to increase pH, cation exchange capacity [6], nutrient availability and to decrease nitrate [7]. RH have also been used as bedding material and feed for livestock [8], in energy generation such as ethanol, biogas and direct combustion [9] as well as for production of fuel briquettes [10]. Elsewhere, RH have been employed to remove various pollutants from water, including dyes, phenols, organic compounds, pesticides, inorganic anions, and heavy metals [11–13]. Through the pyrolysis process, RH can also be converted to bio-oil, a fuel that has gained popularity due to being a possible alternative to fossil fuels. Pyrolysis is a process of thermally decomposing organic material in absence of oxygen [14]. Slow pyrolysis is employed to thermally modify the organic material to maximize char yield while minimizing the bio-oil produced [15]. It takes place at a temperature of 400–500 °C, long residence time (>5 min) and low heating rates <10 °C/s [16,17]. Fast pyrolysis is done using moderate to high heating rates (10–100 °C/s) with bio-oil being the main product [18]. On the other hand, flash pyrolysis is an extremely rapid process with high heating rates varying

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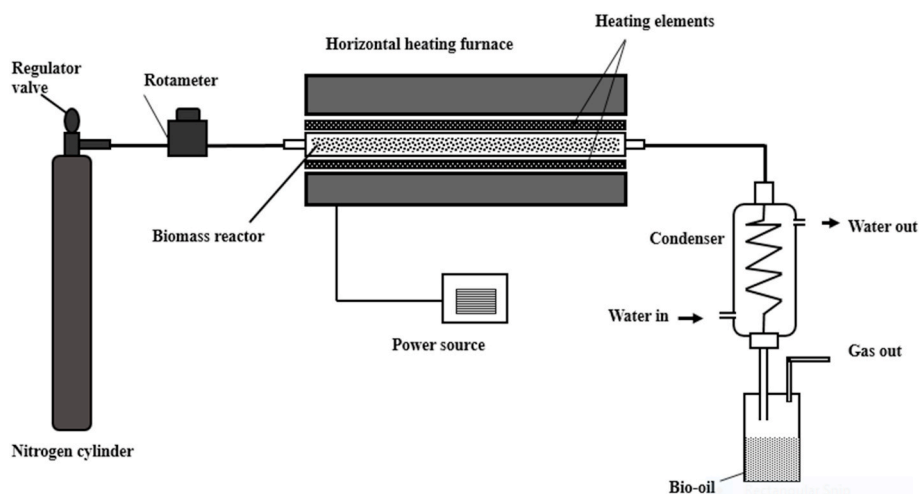


Fig. 1. Setup used during bio-oil production experiments.

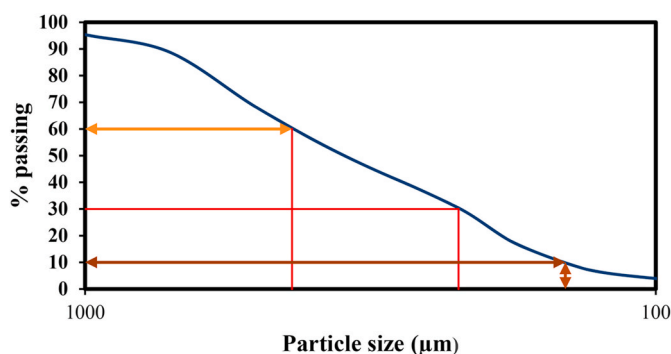


Fig. 2. Particle size distribution of the ground treated rice husks.

Table 1

Proximate composition of the raw and treated rice husks.

Proximate composition					
Sample	% Moisture	%Ash content	%Volatiles on dry basis	% Fixed carbon	
Raw rice husks	11.50 ± 0.20	22.91 ± 0.15	60.50 ± 0.16	13.76 ± 0.13	
NaOH treatment + warm water washing	11.76 ± 0.40	1.82 ± 0.30	78.30 ± 0.30	17.10 ± 0.10	
Ultimate composition					
	C	H	S	N	O (as difference)
Raw rice husks	34.79 ± 0.15	5.86 ± 0.01	0.21 ± 0.01	0.79 ± 0.00	58.35 ± 0.73
NaOH treatment + warm water washing	42.98 ± 0.24	7.34 ± 0.07	0.18 ± 0.03	0.63 ± 0.01	48.87 ± 0.06

from 100 to 10,000 °C/s and short residence duration [19]. The main products of flash pyrolysis are gases and bio-oil. Several studies on RH thermochemical conversion route to bio-oil have been conducted in the recent past. For example, Das & Goud [20] studied pyrolysis of RH characterized with 57.8% volatile matter and reported maximum bio-oil yield of 35.5 wt% at optimum temperature of 427 °C. They reported calorific value, ash and water contents of 14.56 MJ/kg, 0.28% and

25.83%, respectively. In another study, Cai et al. [21] achieved a bio-oil yield of 46.9 wt% through fast pyrolysis at 500 °C with water content of 13.39%. In an earlier study by Ji-lu [22], RH were pyrolysed at temperatures between 420 °C and 540 °C in a fluidized bed and the highest bio-oil yield of 56 wt% was obtained at 465 °C. There is need to ensure that the produced bio-oil through fast pyrolysis conforms to the acceptable standards of calorific value, ash and water contents to enhance its acceptance [23]. Establishing mathematical models by evaluating multiple process parameters, and their interactions using quantitative experimental data effectively optimizes complex production platforms in a statistical way [24,25]. During optimization studies, composite design of experiments has been commonly employed with the choice being supported by the advantages of screening and response surface methodology (RSM) [24–26]. Screening allows identification of significant factors, among those being selected, that have a significant influence on the studied responses [26–28] resultantly reducing the number of experimental trials. Much as research has been conducted to maximize bio-oil production from RH, little has been done to maximize quality of resultant oil. It is necessary to investigate and establish the best possible conditions for adaption during large scale production of quality bio-oil. Therefore, this study set out to model the pyrolysis process for bio-oil production from RH with a goal of maximizing calorific value and minimizing ash and water contents for application as a green energy carrier.

2. Materials and methods

2.1. Sample sourcing and preparation

Rice-husks (RH) were sourced from Zirowe, Luwero located along coordinates 0.67366°N, 32.70035°E in Uganda. Paddy was sun-dried to moisture content of 12–15% wet basis (wb) and milled using a milltop rice milling machine (model SB) leaving RH as waste material. About 10 kg of RH were collected, thoroughly washed with tap water to remove dirt, and any other contaminants present, followed by oven drying at 105 °C for 12 h. Rice husk samples were demineralized by soaking in a 2% w/v NaOH solution for 12 h [29] then washed with warm water at 60 °C for 5 min followed by running tap water for 4 h. This was done to reduce the ash content of rice-husks and resultantly increase the concentration of desired volatile matter for bio-oil production. Demineralized husks were oven dried for 8 h at 105 °C.

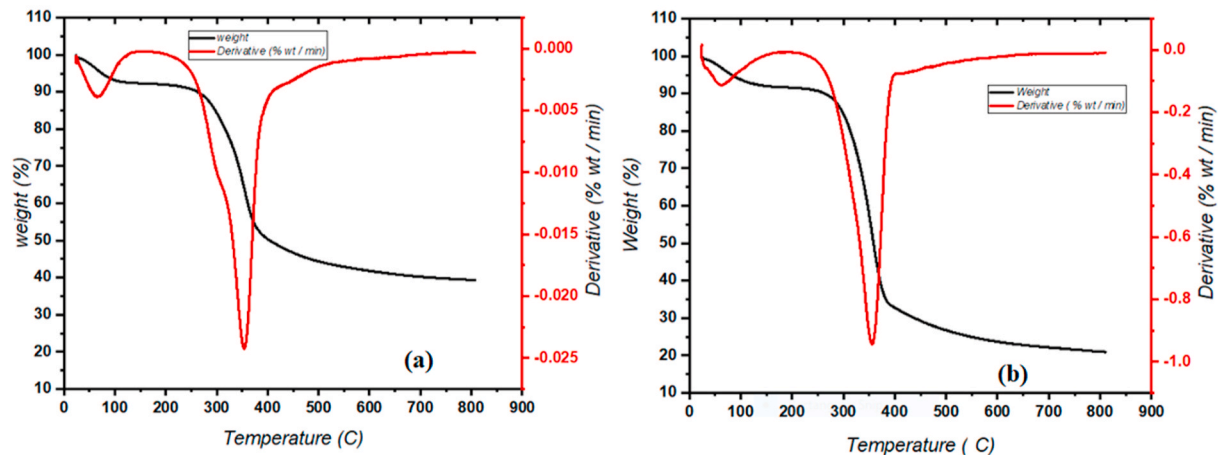


Fig. 3. Thermal decomposition of (a) untreated rice husks, (b) treated rice husks.

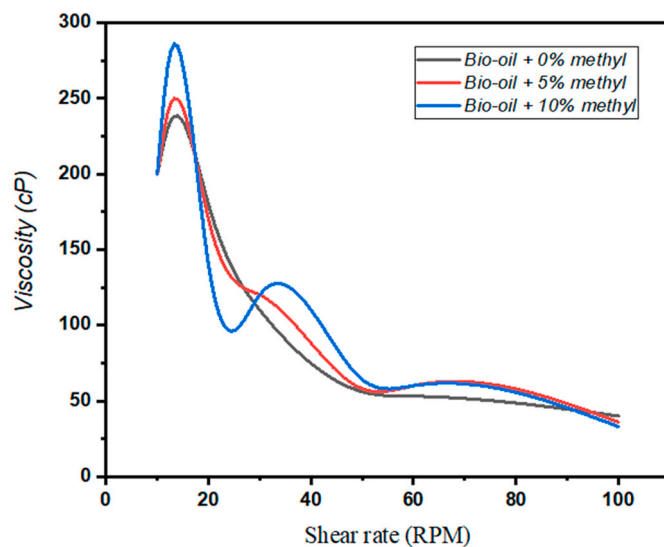


Fig. 4. Change in viscosity with shear stress.

2.2. Rice husk characterization

2.2.1. Particle size distribution

Treated RH were further milled to particle size less than 0.6 mm to promote faster heat and mass transfer during fast pyrolysis. Using BS 410 test Sieves, PAT No-667,924, aperture 1.18 mm, 800, 710, 600, 500, 450, 300, 250, 212, 180, 150, 125, 90 and 63 μm by Endecotts limited, London, sieve analysis was carried out on 200 g of milled RH. Quantities of RH retained on each sieve were measured and recorded to help in determining the particle size distribution.

2.2.2. Proximate analysis and heating value

Ultimate composition of rice-husks was determined using a CHS-ON analyzer. The proximate analysis of rice husks was determined using an ELTRA Thermostep thermogravimetric analyzer (TGA), according to ASTM-D7582-15. This method allows for sequential determination of moisture, volatiles, ash content and fixed carbon in a single analysis. In this method, standard operating procedure (SOP) in the computer was selected. Rice husk samples were weighed by the integrated detection balance. After one sample had been weighed, the carousel automatically rotated to the next position and the next registered sample was then being weighed in the crucible. The TGA experiments were carried out from 25 to 920 $^{\circ}\text{C}$ with a heating rate of 20 $^{\circ}\text{C}/\text{min}$. High-purity com-

Table 2

Design of experiment, variable factors and responses.

Run	Factor 1	Factor 2	Factor 3	Response 1	Response 2	Response 3	Response 4
	A (Temperature, $^{\circ}\text{C}$)	Heating rate $^{\circ}\text{C}/\text{h}$	Holding time, s.	Y1 (Bio-oil Yield, %)	Y2 (Heating Value, MJ/kg)	Y3 (Water Content, %)	Y4 (Ash Content, %)
1	400	9750	1800	29.9	21.4	25.1	0.150
2	525	7875	1200	33.8	22.4	23.4	0.152
3	525	7875	1200	32.3	22.6	23.8	0.159
4	650	6000	600	35.0	22.9	19.1	0.162
5	400	9750	600	20.6	22.6	25.5	0.152
6	400	6000	600	17.5	20.0	19.9	0.130
7	525	7875	1200	21.3	23.0	23.5	0.160
8	400	6000	1800	28.8	20.7	26.4	0.140
9	650	9750	600	34.4	24.0	19.6	0.170
10	650	9750	1200	35.0	25.0	19.0	0.160
11	525	7875	1200	32.5	22.8	23.2	0.154
12	650	6000	1800	36.3	24.1	20.0	0.161
13	525	7875	191	16.9	20.3	25.3	0.149
14	735	7875	1200	36.9	23.7	16.6	0.170
15	525	7875	1200	33.5	22.9	23.7	0.160
16	525	11,028	1200	34.4	22.5	19.8	0.153
17	525	7875	2209	41.3	22.9	21.8	0.153
18	315	7875	1200	22.5	18.4	32.1	0.140
19	525	4722	1200	28.1	22.4	26.3	0.150
20	525	7875	1200	33.1	18.8	28.5	0.151

Table 3
Sequential model sum of squares for responses.

(a) Sequential Model Sum of Squares bio oil yield					
Source	Sum of Squares	df	Mean Square	F-value	p-value
Mean vs Total	18226.01	1	18226.01		
Block vs Mean	5.47	1	5.47		
Linear vs Block	645.20	3	215.07	12.83	0.0002
2FI vs Linear	48.90	3	16.30	0.9659	0.4405
Quadratic vs 2FI	12.34	3	4.11	0.1947	0.8974
Cubic vs Quadratic	78.79	4	19.70	0.8844	0.5344
Residual	111.37	5	22.27		
Total	19128.08	20	956.40		
(b) Sequential Model Sum of Squares for higher heating value					
Mean vs Total	9830.40	1	9830.40		
Block vs Mean	6.03	1	6.03		
Linear vs Block	34.87	3	11.62	10.84	0.0005
2FI vs Linear	1.61	3	0.5378	0.4460	0.7246
Quadratic vs 2FI	2.18	3	0.7250	0.5307	0.6724
Cubic vs Quadratic	2.75	4	0.6872	0.3599	0.8281
Residual	9.55	5	1.91		
Total	9887.38	20	494.37		
(c) Sequential Model Sum of Squares for water content					
Mean vs Total	10694.39	1	10694.39		
Block vs Mean	16.94	1	16.94		
Linear vs Block	154.01	3	51.34	8.04	0.0020
2FI vs Linear	15.58	3	5.19	0.7770	0.5291
Quadratic vs 2FI	17.69	3	5.90	0.8488	0.5013
Cubic vs Quadratic	49.93	4	12.48	4.96	0.0544
Residual	12.58	5	2.52		
Total	10961.11	20	548.06		
(d) Sequential Model Sum of Squares for ash content					
Mean vs Total	0.4702	1	0.4702		
Block vs Mean	3.284E-06	1	3.284E-06		
Linear vs Block	0.0014	3	0.0005	18.72	<0.0001
2FI vs Linear	0.0002	3	0.0001	5.95	0.0100
Quadratic vs 2FI	0.0000	3	0.0000	0.9886	0.4409
Cubic vs Quadratic	0.0001	4	0.0000	1.41	0.3523
Residual	0.0001	5	0.0000		
Total	0.4719	20	0.0236		

pressed air was used for cleaning the crucibles and chamber prior to TGA experiments. Nitrogen gas was used as the purge gas during the analysis to create an oxygen free atmosphere during moisture and volatile matter determination. High purity oxygen was used during the ash determination stage. The Eltra thermostep thermogravimetric analyzer was calibrated using calibration standard coal 92,511-3030 Lot 20131211 B with informative values for moisture wt% wb, ash content wt% db. And volatile matter wt.% db. Of 4.0, 6.5 and 35.9, respectively. The moisture content (wt.%, wb), volatile matter (wt.% db.), ash content (wt.% db.) and fixed carbon (wt.% db.) of the samples were calculated using Equations (1)–(4).

$$\text{Moisture content} = \frac{A - B}{A} \times 100 \quad (1)$$

$$\text{Volatile matter} = \frac{B - C}{B} \times 100 \quad (2)$$

$$\text{Ash content} = \frac{D}{B} \times 100 \quad (3)$$

$$\text{Fixed carbon} = 100 - (\text{moisture content} + \text{volatile matter} + \text{ash content}) \quad (4)$$

Where, A is the initial mass of biomass (g), B is mass (g) after drying at 105 °C, C is mass (g) after devolatilization, D is mass (g) of ash. The calorific value of rice husks was determined using a bomb calorimeter (Gallenkamp Auto Bomb Serial Number-SG96/02/536, UK) following ASTM E711–87 (2004) standard procedure.

2.3. Response surface methodology design

Response surface methodology was employed to investigate the optimum conditions for pyrolysis of rice husks to obtain maximum bio-oil yield and quality. Temperature, heating rate and holding time in the ranges of 400–650 °C, 6000–10,000 °Ch⁻¹ and 600–1800 s, respectively were employed as the input variables for a three factor, two-level Central Composite Design (CCD). The input variables together with their respective ranges were chosen based on literature. Using Stat-Ease-Design-Expert 11.1.2.0 software, 20 experimental runs as calculated in Equations (5) and (6) [29–31] were planned in a randomized order to minimize the effects of the uncontrolled factors. The experimental runs consisted of 14 non center points (factorial points, axial points), and replicates at the 6 center points.

$$N = 2^n + 2n + n_c \quad (5)$$

$$N = 2^3 + 2(2) + 8 = 20 \text{ runs} \quad (6)$$

Where;

N is the total number of experiments that were performed, n is the number of process variables (temperature, heating rate, holding time (3)), and n_c is the number of replicates at the center points (8). The center points were employed to determine the experimental error and the reproducibility of the data.

The responses that were optimized are; the bio-oil yield, calorific heating value, water and ash contents of the bio-oil. The mathematical relationships between the input variables and the responses were modeled using a polynomial according to Equation (7) [30,32].

Table 4

Analysis of variance for the reduced bio-oil yield and HHV models the reduced water and ash content models.

Source	Sum of squares	df	Mean square	F-value	p-value (Prob > F)	Remarks
(a) ANOVA for response surface reduced linear model for bio-oil yield						
Model	633.03	2	316.51	19.21	<0.0001	Significant
A-Temperature	339.04	1	339.04	20.58	0.0003	
C-Holding Time	293.99	1	293.99	17.85	0.0006	
Residual	263.58	16	16.47			
Lack of Fit	161.59	12	13.47	0.5281	0.8237	not significant
Pure Error	101.99	4	25.50			
Cor Total	902.08	19				
(b) ANOVA for response surface reduced quadratic model for higher heating values						
Model	30.05	1	30.05	24.45	0.0001	Significant
A-Temperature	30.05	1	30.05	24.45	0.0001	
Residual	20.90	17	1.23			
Lack of Fit	12.33	13	0.9488	0.4433	0.8809	not significant
Pure Error	8.56	4	2.14			
Cor Total	56.98	19				
(c) ANOVA for response surface reduced linear model for water content						
Model	150.16	1	150.16	25.62	<0.0001	Significant
A-Temperature	150.16	1	150.16	25.62	<0.0001	
Residual	99.62	17	5.86			
Lack of Fit	87.91	13	6.76	2.31	0.2176	not significant
Pure Error	11.71	4	2.93			
Cor Total	266.72	19				
(d) ANOVA for response surface reduced quadratic model for ash content						
Model	0.0016	6	0.0003	21.60	<0.0001	Significant
A-Temperature	0.0012	1	0.0012	100.43	<0.0001	
B-Heating Rate	0.0001	1	0.0001	11.34	0.0056	
C-Holding Time	6.889E-09	1	6.889E-09	0.0006	0.9814	
AB	0.0001	1	0.0001	8.22	0.0141	
AC	0.0001	1	0.0001	4.19	0.0631	
BC	0.0001	1	0.0001	5.44	0.0380	
Residual	0.0001	12	0.0000			
Lack of Fit	0.0001	8	0.0000	0.9505	0.5614	not significant
Pure Error	0.0001	4	0.0000			
Cor Total	0.0017	19				

Table 5Standard deviation, R²-value, adjusted R²-value, predicted R²-value, and adequate precision.

Statistical parameter	Bio-oil yield	Higher heating value	Water content	Ash content
Standard deviation	4.06	1.11	2.42	0.0035
Mean	30.19	22.17	23.12	0.1533
R ² -value	0.7060	0.5899	0.6012	0.9153
Adjusted R ² -value	0.6693	0.5658	0.5777	0.8729
Predicted R ² -value	0.5434	0.4451	0.4317	0.7186
Adequate precision	10.6022	11.8766	11.46910	16.6268

Table 6

Validation experiments for the proposed models.

	Bio-oil yield (%)	Heating Value (MJ/kg)	Water content (%)	Ash content (%)
95% PI low	34.15	22.11	16.9	0.150
95% PI high	45.68	24.98	23.1	0.164
Mean experimental value	38.13	23.41	18.3	0.156
Predicted value	39.92	23.54	20.0	0.157

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j + \epsilon \quad (7)$$

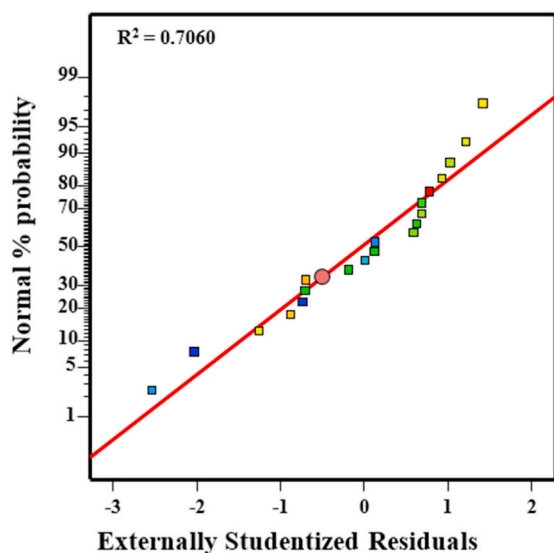
where;

Y is the predicted response (bio-oil yield, calorific heating value, water or ash content), X_i and X_j are the independent variables (temperature, heating rate, holding time), b_0 is the constant coefficient, b_i is the linear coefficient, b_{ii} is the quadratic coefficient, b_{ij} is the interaction coefficient, and ϵ is the error of the model.

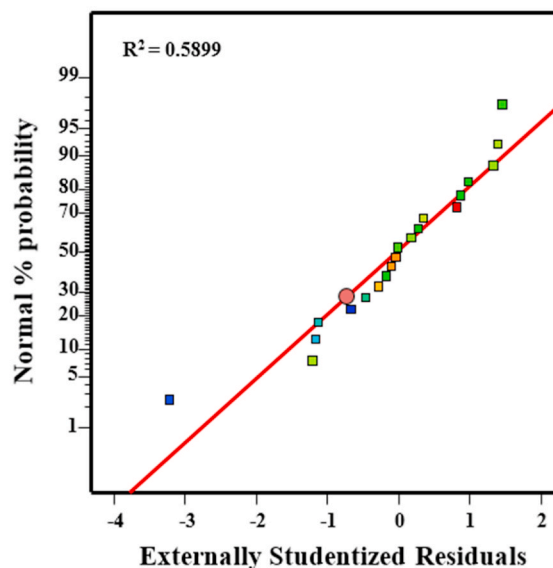
2.4. Bio-oil production and characterization

Bio-oil production experiments set up as illustrated in Fig. 1. About 80 g of ground treated rice-husks were loaded into the reactor of diameter 50 mm and length 500 mm. The reactor was subsequently loaded into a horizontal tube furnace (Carbolite Gero, HTRH 100–300/18). The furnace was purged with nitrogen gas to create an oxygen free environment. The furnace was then set to the pyrolysis temperature (400–650 °C), heating rate (6000–10,000 °C/h), and holding time (600–1800 s). Pyrolysis vapor products were rapidly quenched using water above 55 °C [33] to minimize the amount of moisture trapped in the resultant bio-oil as well as light volatiles. This resultantly improves bio-oil quality in terms of homogeneity, viscosity, stability, odour, and acidity without significantly decreasing the flash point of the bio-oil product [33]. The condensate was collected in a glass flask that allowed escape of the non-condensable gases. The yield of bio-oil and bio-char were measured and recorded. To reduce viscosity, improve stability during storage, improve homogeneity and burning characteristics, and delay the bio-oil phase separation process, 10% concentration of methyl alcohol was added.

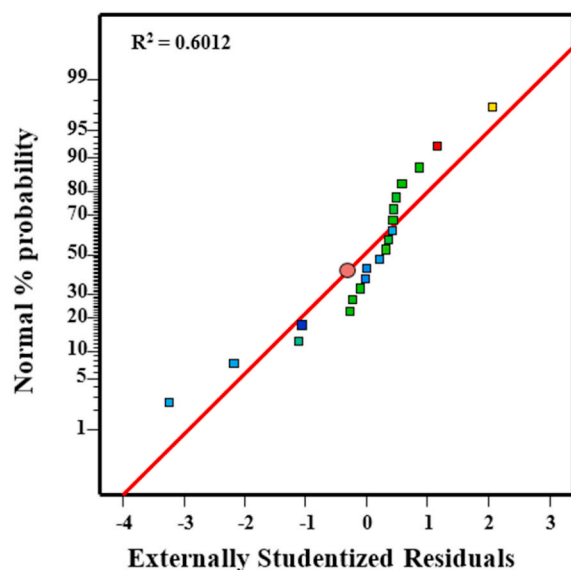
Bio-oil was characterized for higher heating values, viscosity, water content, pH, and ash content. Ash content of bio-oil was determined



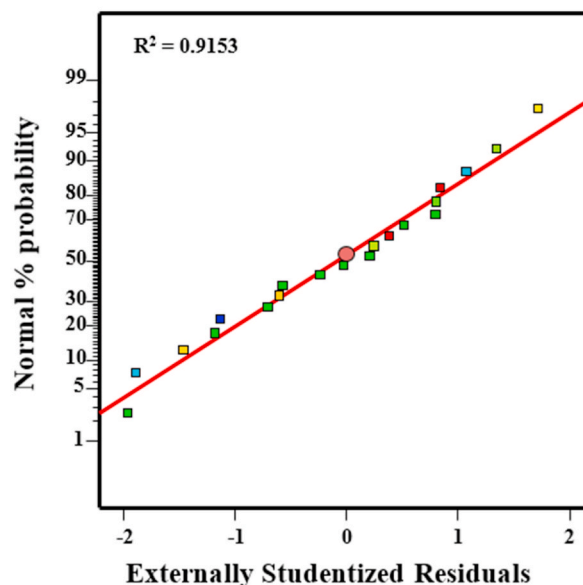
(a)



(b)



(c)



(d)

Fig. 5. Normal probability plot of residues for bio-oil yield (a), higher heating value (b), water content (c) and ash content (d).

using the thermogravimetric method employing an ELTRA Thermostep thermogravimetric analyzer (TGA), according to ASTM-D7582-15 following the procedure indicated in section 2.2.2. Higher heating value and water content were determined using a bomb calorimeter and thermogravimetric method, respectively as outlined in Section 2.2.2. Viscosity was determined using a digital Brookfield DV-E, spindle 5. The spindle was immersed into a 100 mL beaker containing bio-oil. The DV-E spindle was then driven through a calibrated spring. The viscous drag of the fluid was measured by spring deflection. The viscometer was calibrated using viscosity standard fluid with accuracy being $\pm 1\%$. The spindle speed was fixed at 30, 50, 60, 100 rpm and spindle number 5 was used. The pH values of the different samples of bio-oil collected were

determined using a portable pH meter (HQ 30 d Flexi) at room temperature. Bio-oil generated at optimum conditions was characterized for functional surface groups using the Bruker ALPHA II Compact FT-IR Spectrometer with IR spectra in the range of $4000 - 400 \text{ cm}^{-1}$. To determine the different components in the bio-oil, Agilent 7000D triple quadrupole GC/MS system was used to carry out gas chromatography and mass spectrometry.

2.5. Optimization and model validation

The numerical optimization method in Design Expert software was selected to optimize the pyrolysis process conditions. The optimization

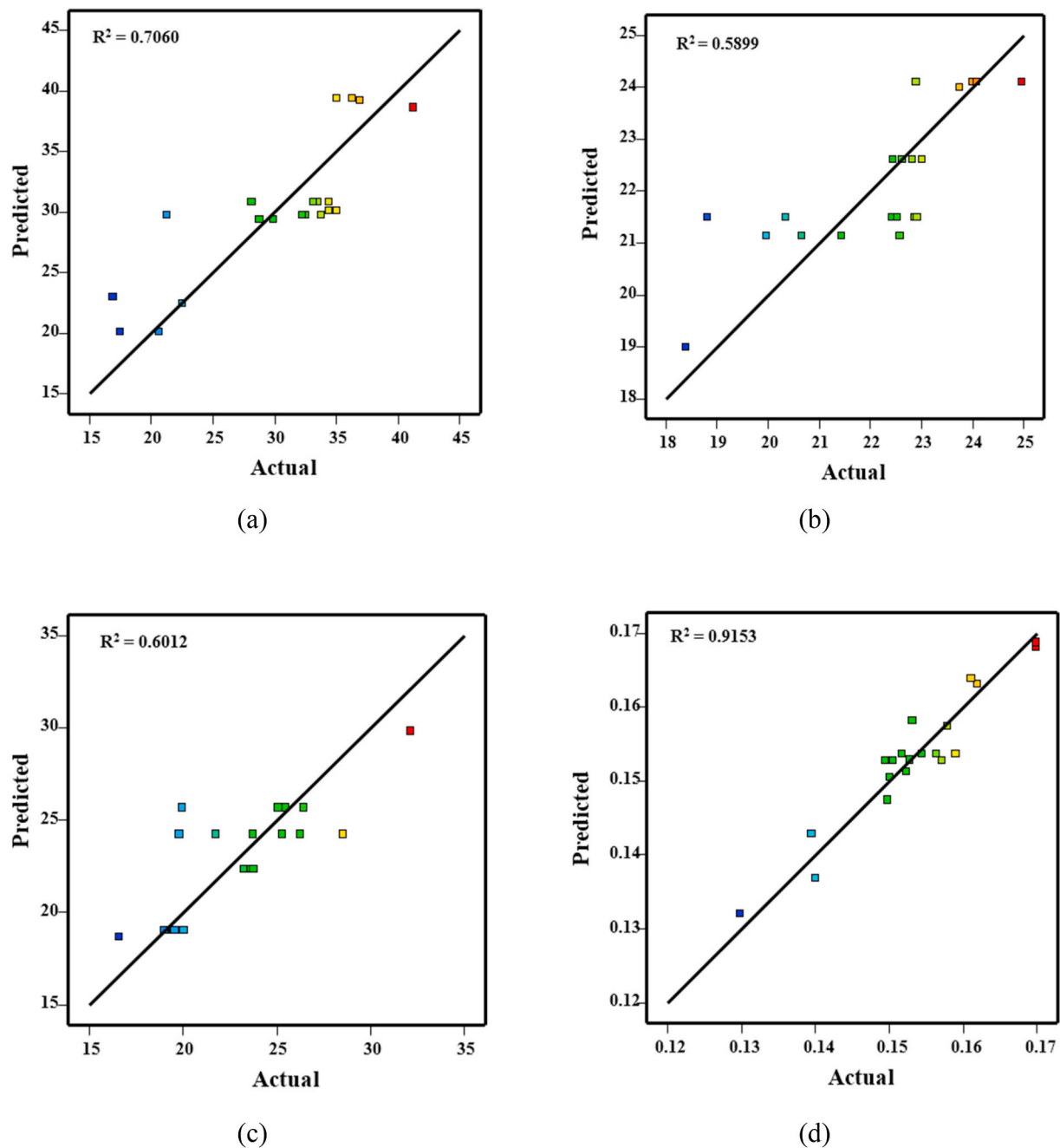


Fig. 6. Predicted values versus experimental values for bio-oil yield (a), higher heating value (b), water content (c) and ash content (d).

criteria were maximization of bio-oil yield and heating value, while minimizing ash and water contents. The values for each of the pyrolysis process parameters temperature, heating rate and holding time were varied within the ranges of 400–650 °C, 6000–10,000 °Ch⁻¹ and 600–1800 s, respectively. Design-Expert software sought for a combination of factors that simultaneously satisfied requirements placed on each of the responses and factors. Obtained models were validated by conducting the respective experiments under optimum pyrolysis conditions attained. Experimental values acquired were compared with model predicted values. The effects of pyrolysis conditions (temperature, heating rate and holding time) on yield and quality of bio-oil were assessed using the surface plots. The relationships between variables were also assessed using these plots. Bio-oil characterization data analyzed in ANOVA to determine the effect of pyrolysis variables on the quality of bio-oil produced in respect to its water and ash content.

3. Results and discussion

3.1. Characteristics of raw and treated rice husks

3.1.1. Proximate analysis

Proximate and ultimate composition of untreated and treated rice husks are shown in Table 1. Ash content of raw rice husks obtained in this study is in agreement with reports from previous studies [34–36]. Rice husks in this study had up to 22.87% ash content wt on dry basis (db.). This ash content was too high compared to the desired less than 5% wt on db for bio-oil production as recommended by Menya et al. [37]. Untreated rice husks had a relatively high moisture and volatile matter content of 11.5% wt on wet basis (wb), and 59.63% db., respectively. This high volatile matter supports bio-oil production as the volatiles directly contribute to the make-up of the pyrolysis liquid

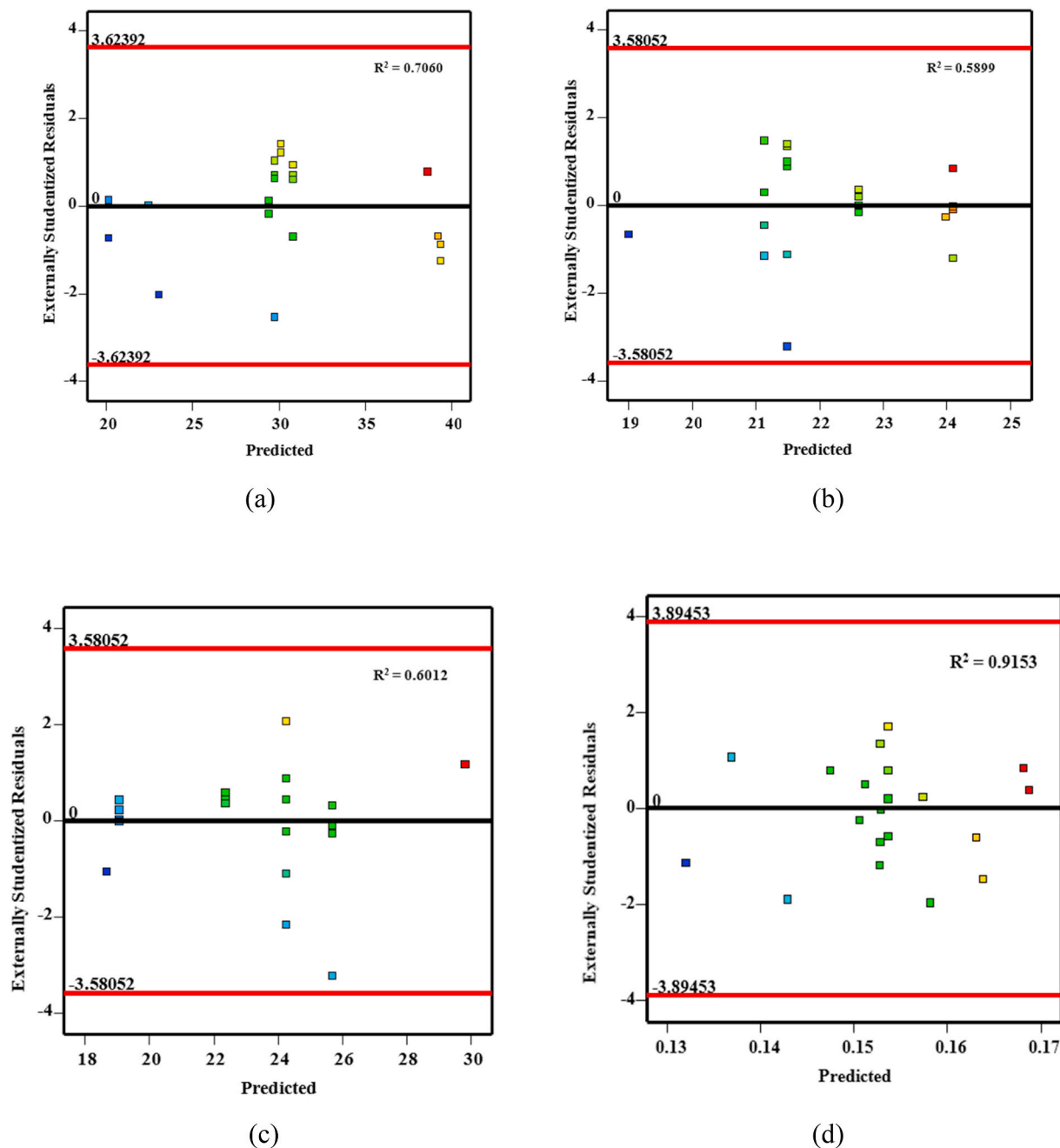


Fig. 7. Residues versus predicted for bio-oil yield (a), higher heating value (b), water content (c) and ash content (d).

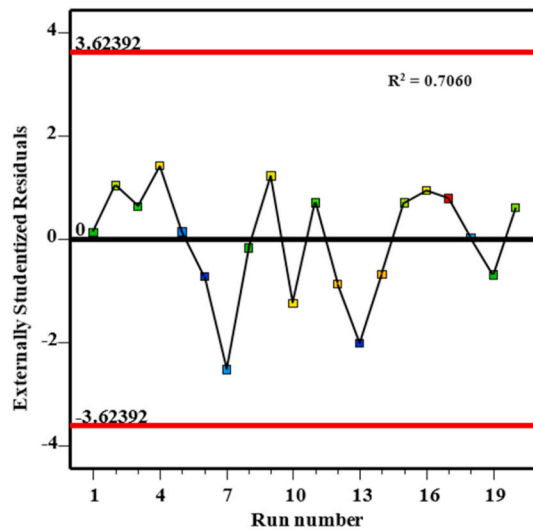
product. However, for high yield and quality of pyrolysis bio-oil, the deleterious high moisture and ash content needed to be reduced to increase the energy density, heating value and reduce viscosity of the product.

Treatment using 2% NaOH w/v solution (RH: NaOH 1:8) led to a reduction in ash content of >92% as well as an increase in the volatile matter of about 30%. An increase in the rice husk fixed carbon was recorded at > 24%. This could be attributed to removal of ash content which resultantly increases the concentration (density) of fixed carbon present. Therefore, for the aforementioned positive reasons, treatment with NaOH solution was adopted throughout the study.

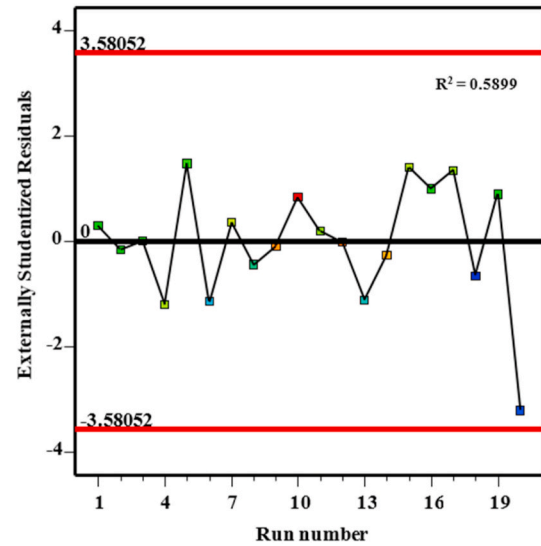
3.1.2. Particle size distribution

Sieve analysis presented 15.9% of the ground rice husks to be larger than 600 μm . The desired size of <500 μm contributed 84.1% of the total

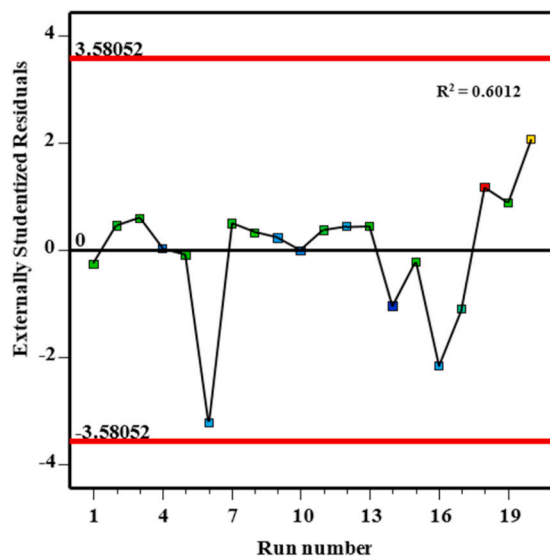
mass with 6.4% being fines <100 μm in particle size. After grading, the particle size D_{10} at which 10% of the rice husks are finer was 144 μm whereas that at which 60% were finer, D_{60} , was at 433.9 μm as can be observed in Fig. 2. 30%, D_{30} , of the rice husk was finer than 221.6 μm size. To be considered a uniform mix and well graded, the uniformity coefficient and coefficient of curvature should be < 4.0 and close to 1 respectively [38]. The coefficient of uniformity (CU) was determined as the ratio of D_{60} to D_{10} and was calculated to be 3.013 which implied a uniform mix of particles [38,39]. The coefficient of curvature (CC) calculated as the square of D_{30} divided by the product of D_{60} and D_{10} was determined as 0.786. This implied that the rice husks particle sizes did not have much variation; with most of the particles falling between 0.144 and 0.434 μm . For purposes of bio-oil production, the little variation of the already broken down particles promotes fast heat transfer during fast pyrolysis [40]. This low variation is due to the poor



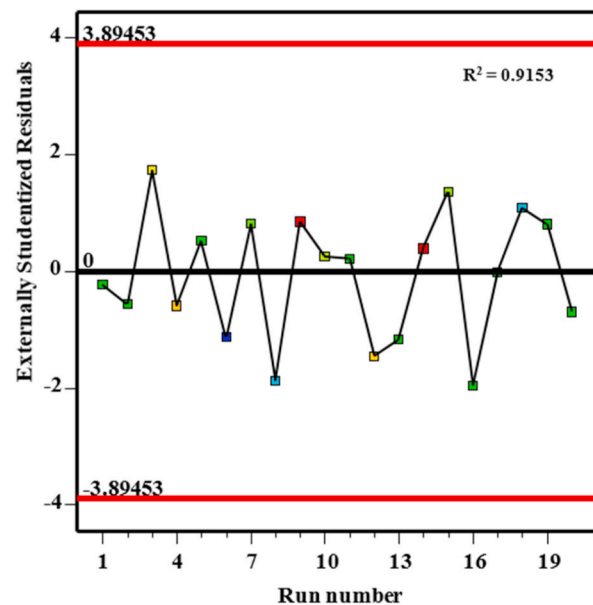
(a)



(b)



(c)



(d)

Fig. 8. Studentized residual versus run number for bio-oil yield (a), higher heating value (b), water content (c) and ash content (d).

grindability of rice husks. Rice husks are difficult to grind due to their high elasticity [38] and possession of fibrous compounds [37].

3.1.3. Thermal decomposition analysis of untreated and treated rice husk

Thermal behavior is illustrated in the TG/DTG curves in Fig. 3(a and b). The untreated rice husk curves show that thermal decomposition occurs in three distinct temperature zones. This is typical of lignocellulosic biomass [41]. The first zone starts from room temperature 25–105 °C, where about 6.5% of the total mass was lost due to evaporation of the water in the rice husk biomass. This zone extends to about 155 °C however at a reduced mass loss rate implying that the rice husks still had hemicellulose, cellulose and lignin intact. In the second phase,

more noticeable devolatilization starts at about 160 °C and continues up to about 376 °C at a much faster mass loss rate. About 40.4% mass is lost in the second phase. The maximum thermal degradation (DTG peak) occurs at 353 °C. The d-half temperature where about 50% wt of the loaded rice husk mass had decomposed was at 403 °C. The longer decomposition temperature range (220–350 °C) of hemicellulose is due to the presence of acetyl groups in its amorphous and random structure made of ordered micro fibrils making it more thermally stable as compared to cellulose (315–400 °C). In the third temperature zone, degradation started at around 400 °C up to 850 °C with mass loss of about 13.8% on dry basis. Slow decomposition of lignin takes place in this phase. The slow rate is due to the structure of lignin consisting of a

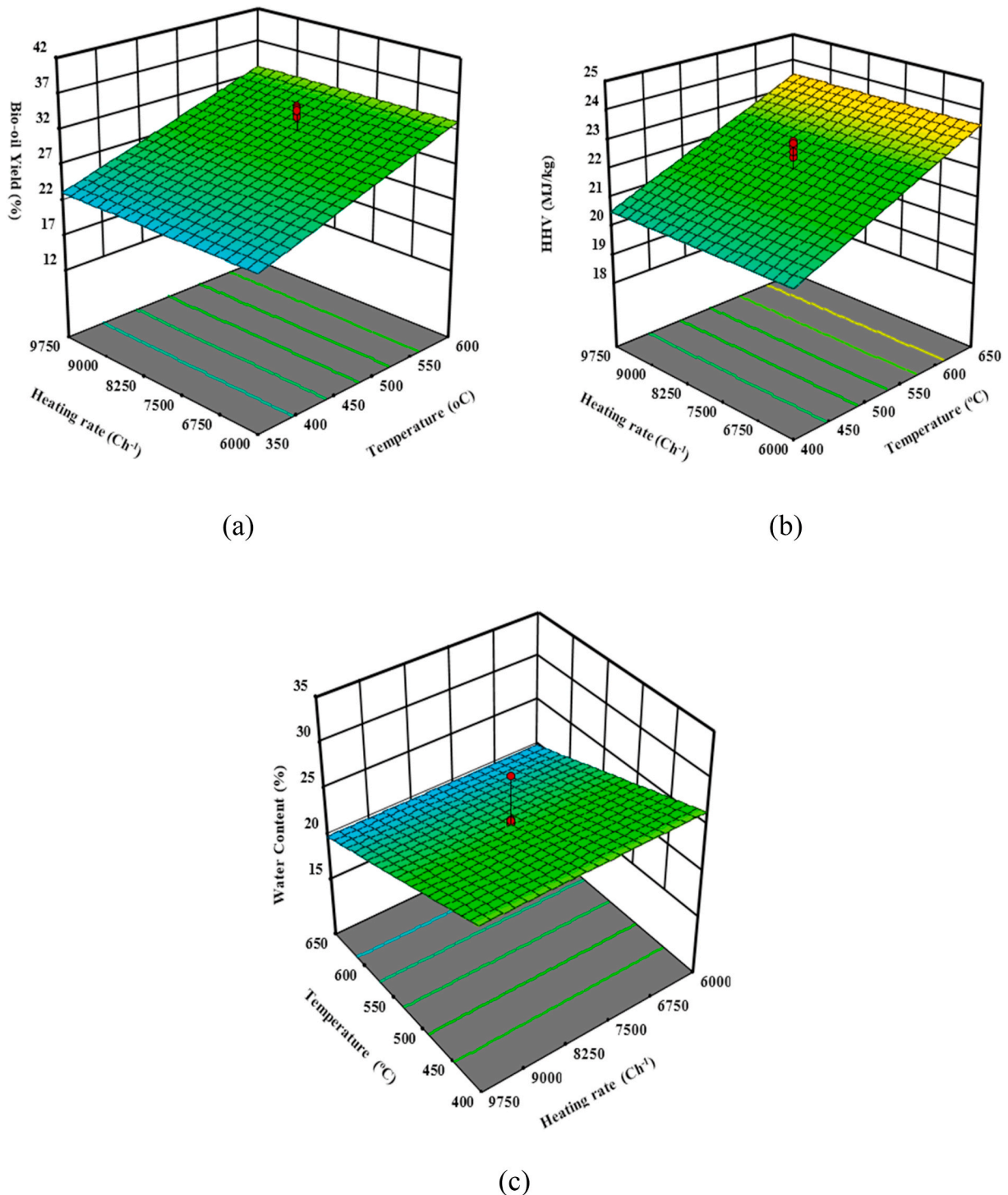


Fig. 9. Effect of temperature and heating rate on (a) bio-oil yield, (b) higher heating value, (c) bio-oil water content d) Ash content.

complex network of cross linked aromatic molecules that are difficult to decompose thus their thermal stability. Incombustible matter was left at the end of the third phase of about 39.3 wt db.

Treated rice husk curves also showed that thermal decomposition occurs in three temperature zones as shown in Fig. 3 (b). The first zone starts from room temperature of 25 °C–105 °C, where about 4% wt mass was lost due to evaporation of the water absorbed by the rice husk. This zone extends to about 130 °C however at a reduced mass loss rate implying that the rice husk hemicellulose, cellulose and lignin were still not influenced. In the second phase, more pronounced devolatilization starts at about 130 °C up to about 380 °C at a much faster mass loss rate.

About 55.1% wt mass is lost during this phase. The d-half temperature where about 50% wt of the loaded rice husk mass had decomposed was at 359 °C. The maximum thermal degradation (DTG peak) occurs at 355 °C. In the third phase, 13.6% mass is lost leaving incombustible matter of about 20% wt. Db. Similar to hemicellulose decomposition of untreated husks, the longer temperature range (220–350 °C) is due to the presence of acetyl groups in its amorphous and random structure made of ordered micro fibrils [42] making it more thermally stable as compared to cellulose (315–400 °C) [43].

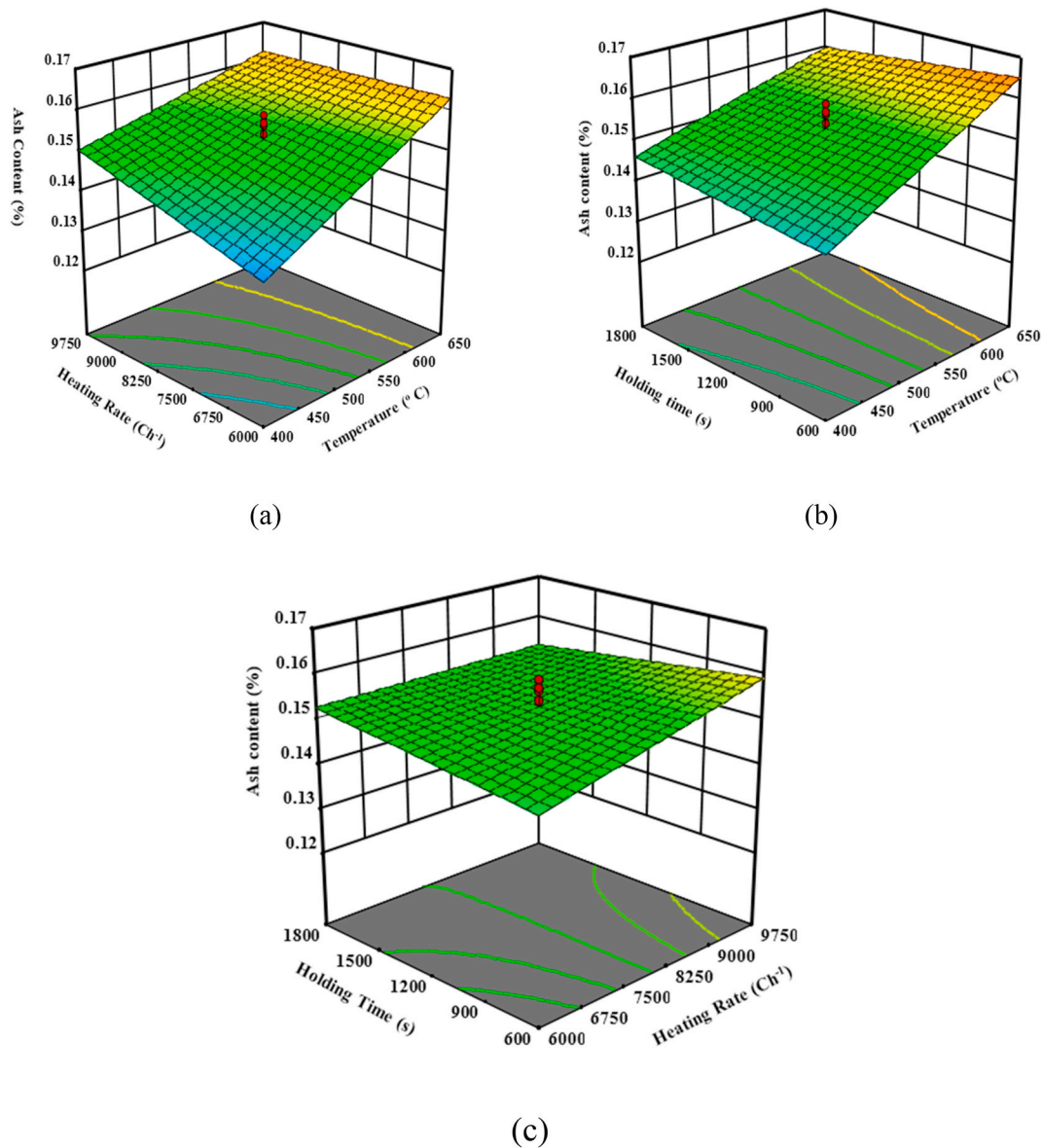


Fig. 10. Effect caused on to bio-oil ash content by (a) temperature and heating rate, (b) temperature and holding time, (c) heating rate and holding time.

3.2. Bio-oil characterization

3.2.1. pH of bio-oil

For all experimental runs performed in the temperature range of 400–650 °C, heating rate 6000–10,000 °Ch⁻¹, and holding time 300–600 s, the resultant bio-oil had pH falling between 2 and 3. This implies that the bio-oil comprises of substantial amounts of acidic compounds [44]. This acidity also implies that the bio-oil is corrosive [45] and extremely severe at elevated temperature of as low as 70 °C due to its oxygen-rich and organic nature [46].

3.2.2. Viscosity

Viscosity tests were performed to determine the fluidity property so as to give a foresight into the stability of bio-oil fuel during storage. As illustrated in Fig. 4, the viscosity was in the range of 20–300 cP (cP). This falls in the range of 25–1000 cP, recommended for bio oils [47]. The viscosity dropped as shear rate rose, both for bio-oil alone and when different quantities of methyl alcohol were added. This implies that the bio-oil is a non-Newtonian fluid [48,49] where constant viscosity is independent of stress. The interfacial films surrounding bio-oil droplets

that prevent them from coalescence are destroyed at high shear rates [50]. With sharp increase in shear rates, the water and oil phases separated.

3.3. Development of regression model equations

Corresponding experimental values for each of the responses bio-oil yield, HHV, water and ash content are shown in Table 2.

From Table 2, bio-oil yield, higher heating value, water content, and ash content values ranged from 16.9 to 41.3%, 18.4–25.0 MJ/kg, 16.6–32.1%, and, 0.130–0.170%, respectively. In order to find the best fit for each of the responses, the respective sequential model sum of squares was considered (see Table 3). From each of these, the highest order polynomial, where the additional terms are significant, and the model is not aliased was suggested by the Design-Expert software and consequently selected.

Linear vs block models were found to best fit the responses of bio-oil yield, heating value and water content respectively. The two factor interaction (2FI) model was found to best describe the ash content response. The Linear vs block model had a lower *P*-value (<0.0001),

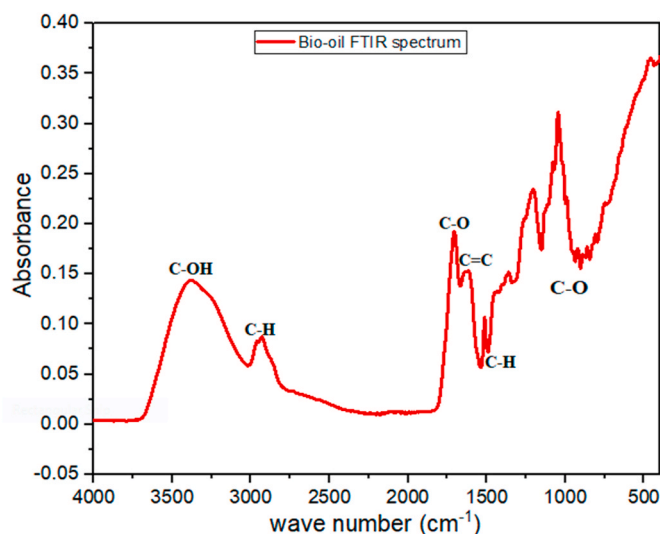


Fig. 11. Fourier transformation infrared spectrum of bio-oil generated at optimum conditions.

higher sum of squares and F-value as compared to the 2FI vs linear model, however, the former had a lower R^2 -value ($R^2 = 0.7892$) while the latter had a high value of 0.9153. This implied that the selected 2FI vs linear model is able to explain better (91.5%) the variance between the predicted and experimental values. In terms of coded factors, the response surface reduced linear and 2FI models corresponding to bio oil yield (Y_1), higher heating value (Y_2), water content (Y_3) and ash content (Y_4), after excluding the insignificant terms are given in Equations (8)–(11), respectively.

$$Y_1 = +30.29 + 4.98A + 4.64C \quad (8)$$

$$Y_2 = +22.06 + 1.48A \quad (9)$$

$$Y_3 = +23.31 - 3.32A \quad (10)$$

$$Y_4 = +0.1532 + 0.0095A + 0.0032B - 0.0035AB - 0.0025AC - 0.0029BC \quad (11)$$

Where A, B and C are temperature, heating rate and holding time in $^{\circ}\text{C}$, $^{\circ}\text{Ch}^{-1}$ and s respectively. The positive sign (+) indicates synergistic effect, while the negative sign (−) indicates the antagonistic effect of the factor on the given response.

3.3.1. Analysis of variance

The results of ANOVA are summarized in Table 4. The model F-values of 19.21, 24.45, 25.62 and 21.60 corresponding to the linear models for bio-oil yield, heating value, water and, ash content respectively, imply that the developed models are significant with p -values less than 0.05. For all the developed models, there is only a 0.01% chance that a model F-value that larger could occur due to noise. Lack of fits for the models were found to be non-significant with p -value greater than 0.05. This suggests that the developed models fit well the experimental data, and can therefore adequately describe the functional relationship between experimental factors and response variables [29]. Model terms are significant for p -values less than 0.05, and not significant for p -values greater than 0.10. Based on this, the significant terms for the reduced linear model corresponding to bio-oil yield were temperature and holding time with F-values of 20.58 and 17.85, respectively. The significant term for the response surface reduced linear model corresponding to higher heating value was temperature with F-value 24.45 (see Table 5). Temperature with an F value of 25.62 was also the significant term for the response surface reduced linear model corresponding to water content (see Table 6). For the ash content model,

Table 7

Chemical compounds in bio-oil generated at optimum pyrolysis.

Retention time (min)	Compound name	Formula	% peak area
8.16	2-Butanone, 3-methoxy-3-methyl-	$\text{C}_6\text{H}_{12}\text{O}_2$	1.11
8.16	Propane, 2-methoxy-2-methyl-	$\text{C}_5\text{H}_{12}\text{O}$	1.50
8.29	Benzaldehyde, 3-hydroxy-4-methoxy-	$\text{C}_8\text{H}_8\text{O}_3$	10.99
8.36	1,3-Benzenediol, 4,5-dimethyl-	$\text{C}_8\text{H}_{10}\text{O}_2$	1.78
8.40	3-Hydroxy-4-methylbenzaldehyde	$\text{C}_8\text{H}_8\text{O}_2$	0.03
8.51	4-Formyl-3,5-dimethyl-1H-pyrrole-2-carbonitrile	$\text{C}_8\text{H}_8\text{N}_2\text{O}$	1.35
8.56	Acetic anhydride	$\text{C}_4\text{H}_6\text{O}_3$	0.54
8.74	3,5-Dimethoxy-4-hydroxytoluene	$\text{C}_9\text{H}_{12}\text{O}_3$	3.60
8.86	Phenol, 2-methoxy-6-(2-propenyl)-	$\text{C}_{10}\text{H}_{12}\text{O}_2$	5.40
8.89	[1,4]Oxathiine-2-carboxylic acid, 5,6-dihydro-	$\text{C}_5\text{H}_6\text{O}_3\text{S}$	0.05
9.44	Apocynin	$\text{C}_9\text{H}_{10}\text{O}_3$	6.65
9.76	Ethanone, 1-(2,5-dihydroxyphenyl)-	$\text{C}_8\text{H}_8\text{O}_3$	1.29
9.85	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	$\text{C}_9\text{H}_{10}\text{O}_4$	4.79
10.08	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$\text{C}_{10}\text{H}_{12}\text{O}_3$	13.10
10.48	Dodecanoic acid	$\text{C}_{12}\text{H}_{24}\text{O}_2$	1.36
10.71	Dihydro-2(3H)-thiophenone	$\text{C}_4\text{H}_6\text{OS}$	0.08
11.00	1-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$\text{C}_{10}\text{H}_{12}\text{O}_3$	2.17
11.21	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	$\text{C}_{11}\text{H}_{14}\text{O}_3$	0.89
11.79	1-Naphthalenol, 2-methyl-	$\text{C}_{11}\text{H}_{10}\text{O}$	0.39
12.19	Benzaldehyde, 4-ethyl-	$\text{C}_9\text{H}_{10}\text{O}$	0.24
12.31	Homovanillic acid	$\text{C}_9\text{H}_{10}\text{O}_4$	2.16
12.34	Benzoic acid, thio-, isopropylidenedehydrazide	$\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}$	0.03
12.47	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	$\text{C}_9\text{H}_{10}\text{O}_4$	1.39
12.60	8-Methyl-5H-pyrrolo [4,3-b]indole	$\text{C}_{12}\text{H}_{10}\text{N}_2$	0.03
13.35	1,3-Dioxolane	$\text{C}_3\text{H}_6\text{O}_2$	1.07
14.05	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	$\text{C}_{10}\text{H}_{12}\text{O}_4$	2.79
14.19	Coniferyl aldehyde	$\text{C}_{10}\text{H}_{10}\text{O}_3$	2.16
14.86	Syringylacetone	$\text{C}_{11}\text{H}_{14}\text{O}_4$	1.90
16.67	2-Propenoic acid, 3-(4-hydroxy-3-methoxyphenyl)-	$\text{C}_{11}\text{H}_{12}\text{O}_4$	1.16
17.37	Hexanedioic acid, mono (2-ethylhexyl)ester	$\text{C}_{14}\text{H}_{26}\text{O}_4$	0.83
20.14	n-Hexadecanoic acid	$\text{C}_{16}\text{H}_{32}\text{O}_2$	6.63
24.54	cis-7-Hexadecenoic acid	$\text{C}_{16}\text{H}_{30}\text{O}_2$	3.18
24.67	trans-13-Octadecenoic acid	$\text{C}_{18}\text{H}_{34}\text{O}_2$	3.78
25.02	Octadecanoic acid	$\text{C}_{18}\text{H}_{36}\text{O}_2$	1.52
28.49	Hexanedioic acid, dioctyl ester	$\text{C}_{22}\text{H}_{42}\text{O}_4$	5.44
30.17	Phthalic acid, di (2-propylpentyl) ester	$\text{C}_{24}\text{H}_{38}\text{O}_4$	8.13
32.36	1,3-Benzenedicarboxylic acid, bis(2-ethylhexyl)	$\text{C}_{24}\text{H}_{38}\text{O}_4$	0.48

temperature, heating rate, holding time were significant terms with F-values of 100.43, 11.34, 0.0006, respectively. Interactions between temperature and heating rate as well as heating rate and holding time were also significant terms for the ash content model with F-values of 8.22, 5.44, and 5.44, respectively.

The goodness of fit of the developed models was evaluated basing on standard deviation, R^2 -value, adjusted R^2 -value, predicted R^2 -value, and adequate precision (see Table 5). The standard deviation corresponding to each of the responses was small, indicating that the developed models are good enough to be employed for prediction. The relatively high R^2 -values indicate that the data satisfactorily fits the developed models. More importantly, the adjusted and predicted R^2 -values corresponding to each of the responses were in reasonable agreement as their difference was less than 0.2. This consequently confirmed the favorability of the developed models. In addition, since signal to noise ratios were found greater than 4, then the developed models can be employed to navigate the design space.

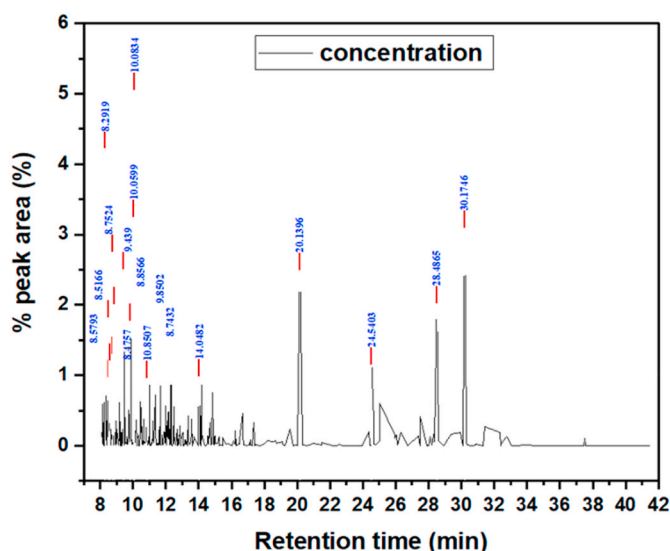


Fig. 12. Chromatogram for bio-oil produced at optimum pyrolysis conditions.

3.3.2. Diagnostics

Normal probability plots of externally studentized residuals, the predicted versus actual values of the responses, as well as plots of externally studentized residuals versus predicted values are shown in Figs. 5–8. These plots were employed to check the adequacy of the fitted models. For a good model, it is recommended that residuals be randomly and normally distributed [51,52]. Fig. 5 shows that the points on the normal probability plots conform to a straight line, confirming normal distribution of the data [53]. The plots of predicted versus actual values of bio-oil yield, higher heating rate, water and ash content shown in Fig. 6, respectively, show minimal divergence of points from the straight line, suggesting that the developed models can be employed to adequately represent the functional relationship between the experimental factors and the response variables [54]. The plots of externally studentized residuals versus predicted values shown in Fig. 7 do not show any particular pattern, suggesting random distribution of the residues, a requirement for a good model.

The plots of studentized residual versus run number (Fig. 8) did not also show any particular pattern, suggesting good data distribution. All data was distributed within the acceptable limits, suggesting no constant error detected [55].

3.3.3. Response surfaces

3.3.3.1. Bio-oil yield. Fig. 9 (a) shows the three-dimensional (3D) response surfaces that were plotted to indicate the interactive effects between heating rate and temperature on bio-oil yield. From the 3D surface plots, it can be seen that the bio-oil yield increased with an increase in both temperature and heating rate affirming the ANOVA results already obtained. This tendency may be attributed to the fact that increase in temperature provides extra energy to break the rice-husk lignin structure [56,57] while higher heating rates favor devolatilization [58,59]. Moreover, the straight contour lines confirm a first-order regression model, where only the main effects of temperature and heating rate had significant influence on bio-oil yield [60]. The interactive effects between the heating rate and temperature did not therefore have significant influence on the bio-oil yield.

3.3.3.2. Higher heating value. Fig. 9 (b) shows the 3D response surfaces that were plotted to show the interactive effects between heating rate and temperature on the heating value of bio-oil derived. It can be seen from the 3D plot that the higher heating value increased with an increase in pyrolysis temperature. This tendency may be attributed to the

decrease in the oxygen content of bio-oil and increased carbon content which positively affect the higher heating rate [61]. Huang et al. [62] reported that bio-oil obtained at low temperatures is mainly composed of alkenes, alkanes, long chain fatty acids, esters, aliphatic nitriles and amides. They further reported that bio-oil acquired at higher temperatures is dominated by shorter aliphatic carbons, light alcohol compounds, ketones and their derivatives as a result of decomposition reactions. From the 3D response plot, heating rate had minimal influence on the energy value of the bio-oil. This may be attributed to experimental heating rate values being relatively close, 100–162.5° Cmin⁻¹ (6000–9750° Ch⁻¹), thus having a negligible effect change on the heating value. With a wide difference in the heating rates, the bio-oil heating value increases due to deoxygenation [63]. The straight contour lines confirm a first-order regression model, where only the main effects of temperature and heating rate had significant influence on heating value [60]. The interactive effects between the heating rate and temperature did not therefore have significant influence on the oils higher heating value.

3.3.3.3. Water content. Fig. 9 (c) shows the 3D response surfaces that were plotted to show the interactive effects between heating rate and temperature on the water content of bio-oil derived. Referring to the 3D surface plot, it can be seen that water content decreased with an increase in pyrolysis temperature. This tendency may be attributed to increased deoxygenation with temperature and since oxygen is one of the water forming compounds, less of the moisture ends up in the bio-oil product [64]. However, the rice husk composition as well as the condensation temperature of the volatiles also influence the water content in the product bio-oil. A condensation temperature >55 °C should be used to avoid trapping moisture along with the target volatiles [65]. The straight contour lines confirm a first-order regression model, where only the main effects of temperature and heating rate had significant influence on water content [60]. The interactive effects between the heating rate and temperature did not therefore have significant influence on the oils water content.

Fig. 10(a–c) shows the 3D response surfaces that were plotted to indicate the interactive effects between pyrolysis parameters on the ash content of bio-oil. Referring to the 3D surface plots, it can be seen that ash content increased with an increase temperature as well as heating rate. This tendency may be attributed to an increase in secondary cracking of volatiles and resultantly higher gas yield, which carries along inorganic material that ends up in the product bio-oil. Again from the 3D surface plots, it can be seen that holding time did not have much influence on ash content, affirming the results already obtained from the ANOVA (see Section 3.4.1). The non-straight contour lines confirmed a second-order regression model [60], which corroborate with the results obtained from the ANOVA. However, the interactive effects between the pyrolysis parameters on ash content were negligible, as can be seen from the non-elliptical or non-saddle nature of the contour plots [66].

3.3.4. Process validation

From model simulation using the numerical optimization method of the Design-Expert software, the optimum pyrolysis conditions were suggested as follows: pyrolysis temperature (650 °C), heating rate (9750 °Ch⁻¹), and holding time (1800 s). If pyrolysis was done at these conditions, the bio-oil yield, heating value, water content, ash content as predicted by the respective developed models are 39.92%, 23.54 MJ/kg, 20% and 0.157% respectively. For validation, predictive capability of the developed models, the optimum pyrolysis conditions suggested were assessed towards the responses of bio-oil yield, heating value, water and ash content. The resultant response values were subsequently compared with the values predicted by the respective models. As a rule of thumb, the mean experimental values must lie within the range of values for 95% prediction interval (PI) low and 95% PI high, for a reliable predictive capability of the developed models, otherwise the model is

negated. In this study, the mean experimental values corresponding to each of the responses lie between the values for 95% PI low and 95% PI high (see Table 6), suggesting that the developed models are valid.

3.4. Further characterization of bio-oil

3.4.1. FTIR spectroscopy

Wave numbers of substantial functional groups were between 3000 and 3500 cm^{-1} as well as between 1000 and 1750 cm^{-1} (see Fig. 11) indicating the existence of C=O, C=C, C-O, C-H, and O-H bonds [67] in bio-oil. The O-H stretching vibrations between 3200 and 3400 cm^{-1} indicate the presence of acids [68] such as acetic acids that are common in bio-oil, phenols and alcohols [49,50]. These are acidic compounds in nature contributing to the overall acidity [69]. On the positive side, phenols and acids have relatively higher heating values compared to other compounds such as aldehydes, esters and ketones [70]. The C-H stretching vibrations between 2800 and 3000 cm^{-1} [71] and the C-H deformation vibrations between 1350 and 1475 cm^{-1} indicate the presence of alkanes [72]. The C-O stretching vibrations with absorbance between 1650 and 1780 cm^{-1} indicate the presence of ketones [73] such as acetol or aldehydes [55,56]. Ketones and aldehydes have low calorific values [74] implying that their contribution to the overall bio-oil energy content is minimal [75]. The absorbance of peaks between 1575 and 1675 cm^{-1} represent C=C stretching vibrations indicative of alkenes [76] and aromatics [58,59]. The overlapping peaks between 900 and 1300 cm^{-1} were due to the presence of primary, secondary, and tertiary alcohols [77] and also phenols due to C-O stretching and O-H deformations of these functional groups. Peaks between 690–900 and 1420–1600 cm^{-1} indicate mono/polycyclic and substituted aromatic groups [78].

3.4.2. Organic compounds

Considering only the peaks of the sufficiently high match factor (75%) with electronic library search routines, the list of compounds present in the bio-oil is presented in Table 7. The percentage peak area for compounds indicates their concentration in bio-oil. The main types of compounds identified in bio-oil are phenols, alcohols, alkanes, ketones or aldehydes, alkenes, esters, as well as aromatics. These can further be classified as furan, alkanes, phenol, acids, esters, hexane, laevoglucose, amide, nitriles, and benzene. These identified compounds are typical of oils extracted from plant matter [79–81].

Considering the percentage peak area, compounds such as; 2-Propenone, 1-(4-hydroxy-3-methoxyphenyl)-, Benzaldehyde, 3-hydroxy-4-methoxy-, Benzene, 1,3-dimethyl-5-propoxy-, Phthalic acid, di (2-propylpentyl) ester, 1,2,4-Trimethoxybenzene, Apocynin, *n*-Hexadecanoic acid, Hexanedioic acid, dioctyl ester, Phenol, 2-methoxy-6-(2-propenyl)-, Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester, *trans*-13-Octadecenoic acid, 3,5-Dimethoxy-4-hydroxytoluene, *cis*-7-Hexadecenoic acid, Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- were the main contributors to the composition of bio-oil generated at optimum pyrolysis conditions. The chemicals identified are similar to those in works on bio-oil characterization by other researchers [71,82–84]. Phenols had the largest concentrations (peak area) which is desired for quality bio-oil [85]. The congested peaks from the chromatogram in Fig. 12 running from 8 to about 15 min-retention time suggest presence of low molecular weight compounds in bio-oil [86] such as esters, aldehydes or ketones which negatively influence stability of the fuel [85]. However, peaks continue to spin over the x-axis (retention time) suggesting that the thermal stability is enhanced an indicator of improved bio-oil quality.

4. Conclusion

1. Pre-treatment of rice husks with 2%w/v NaOH solution resulted in 92% removal of inorganics. This subsequently increased the energy

density as well as volatile matter by 24% wt and 30% wt, respectively.

2. Ground rice husks had a coefficient of uniformity of 3.013 which indicated a uniform mix of particles. The coefficient of curvature was 0.786 implying little particle size variation which was desirable for fast heat transfer.
3. Fast pyrolysis with temperature, holding time, and heating rate in the ranges 400–650 °C, 600–1800 s, 6000–10,000 °C h^{-1} respectively resulted in bio-oil yields of 16–42%.
4. The quality characteristics of bio-oil were; higher heating value (18.5–24.95 MJ/kg), water content (16.6–32.1%), ash content (0.13–0.17%), and pH (2–3). These results fall in the range of standard quality values for bio-oil in published literature where >15 MJ/kg, 20–30%, 0.15–0.25% are the recommended ranges for HHV, water and ash content, respectively. Pyrolysis temperature was found to exhibit the greatest influence over bio-oil yield followed by holding time and lastly heating rate. Optimum pyrolysis conditions were found to be 650 °C, 9750 °C h^{-1} , and 1800s resulting in bio-oil yield, higher heating value, water and ash contents of 38.13%, 23.40 MJ/kg, 18.27% db and 0.156% db respectively.
5. From FTIR results, phenolic compounds were identified as part of the main contributors in the bio-oil which positively affect the quality due to their high calorific values. Gas chromatograph and mass spectrometry results showed peaks continuing to spill up to the maximum retention time indicating improved thermal stability and bio-oil quality.

Credit author statement

Joel Wakatuntu: Conceptualization, Methodology, Writing- Original draft preparation, Peter Wilberforce Olupot.: Data curation, methodology, reviewing and editing Joseph Jjagwe: Visualization, reviewing, editing, Emmanuel Menya: Reviewing and editing. Mackay Okure: Supervision, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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