



Optimization of pyrolysis conditions for char production from rice husks and its characterization as a precursor for production of activated carbon

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Abstract

Response surface methodology was employed to optimize pyrolysis conditions for production of char with maximum yield, fixed carbon content, and with minimum ash content from Uganda's New Rice for Africa (NERICA) 1 rice husk variety. The aim was to obtain rice husk char with more suitable properties as an activated carbon precursor. Mathematical models were developed to explain the relationships between the experimental responses and the pyrolysis parameters of temperature (400–600 °C), heating rate (10–25 °C min⁻¹), and heating period (60–120 min). The optimized rice husk char was further characterized for elemental and proximate compositions, thermal behavior, specific surface area, as well as surface functional groups. Results from the analysis of variance (ANOVA) revealed that the quadratic model best fits each of the responses. Pyrolysis temperature had the greatest influence on each of the responses, followed by heating period, and lastly heating rate. Optimum pyrolysis conditions were found to be temperature (406 °C), heating rate (10 °C min⁻¹), and heating period (60 min), resulting in char yield, fixed carbon, and ash contents of 35.26, 55.39, and 35.01% dry basis, respectively. Compared to raw rice husk, the resulting rice husk char was found more suited as activated carbon precursor, due to its enriched carbon content (60.35%) and specific surface area (123.9 m² g⁻¹). Thermogravimetric analysis of the rice husk char revealed that thermal activation temperatures higher than 400 °C may be required to considerably devolatilize the char, forming a more porous activated carbon.

Keywords NERICA 1 rice husk · Pyrolysis · Optimization · Char yield · Fixed carbon · Ash content

1 Introduction

Pyrolysis is one of the sustainable ways of utilizing biomass waste, as opposed to open dumping and/or burning, which

usually lead to environmental pollution. During this process, biomass is thermochemically decomposed in an inert environment, under temperatures of less than 700 °C [1]. Moisture and volatiles are driven off from the biomass, with the latter having good prospects for utilization as raw materials for synthesis gas production [2], as well as for bio-oil production [3]. On the other hand, the solid carbonaceous residue (char) left behind, can be subsequently utilized as a fuel [4], catalyst for thermochemical cracking of bio-oil and tars [5], soil conditioner [6], adsorbent [7], or as activated carbon precursor [8]. The activated carbon resulting from activation of char could be employed either, as an adsorbent, or as an active material in the preparation of electrodes for high-performance supercapacitors, as well as lithium-ion batteries [9]. Therefore, aside from sustainably disposing of biomass waste, pyrolysis paves way for obtaining sustainable alternative precursors for production of value-added, eco-friendly products [10]. However, careful selection of biomass, as well as control of pyrolysis conditions, is desired, if maximum product yields, and quality are to be obtained [11].

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In char production, a high char yield, low ash content, as well as a high carbon content are important considerations, if the char is to be employed, for instance, as an adsorbent [12], fuel [13], or as an activated carbon precursor [14]. A high char yield enhances the economic feasibility of the pyrolysis process [15], while a high carbon content is linked to a high carbon yield, as well as a high porosity formation, required in most of the above mentioned applications [16]. In char applications as a fuel, a high carbon content is required, since it potentially increases the heating value of char [17]. However, a high ash content could lower the heating value of char, as well as cause agglomeration, and fouling in the components of thermochemical conversion systems [18]. Similarly, the high ash content could hinder the subsequent utilization of char as activated carbon precursor, by obstructing pore development, which consequently leads to activated carbon with low adsorption capacity. Therefore, for successful utilization of char in such applications, a relatively low ash content of char is much desired. Indisputably, by pyrolyzing biomass waste, both the ash and carbon contents of biomass are enriched, while at the same time, the char yield decreases significantly with increasing pyrolysis temperature [19]. This makes the process of maximizing the char yield, carbon content, as well as minimizing ash content of the resulting char somewhat intricate, since the interest region of the pyrolysis variables differ for the different responses [20]. Such complexity of obtaining char with the aforementioned attributes could be solved by employing response surface methodology (RSM); one of the statistical and mathematical tools capable of fitting a quadratic surface analyze interactions between pyrolysis parameters, as well as optimize the significant parameters. Included in the RSM is the analysis of variance (ANOVA), which provides statistical results, as well as diagnostic checking tests, enabling researchers to evaluate the adequacy of the established models. Compared to single factor experiments, RSM approach requires fewer experimental runs, making it less time consuming, as well as less costly [21]. Moreover, by conducting single factor experiments, interaction effects between process variables on the target responses are merely ignored, losing significant information about the experimental process [22]. Some researchers have previously employed RSM to optimize pyrolysis process conditions, for instance, (i) to obtain maximum bio-oil yields from biomass wastes such as rice husks [23] and Mahua press seed cake [24]; (ii) to obtain chars with maximum total organic carbon content, cation exchange capacity, surface area, as well as maximum pore volume and char yield from rice husks, and oil palm empty fruit bunch [1, 25]; (iii) to obtain maximum hydrogen and char yields from oil palm fiber [26]; (iv) to obtain char with low volatile matter, high ash content, high pH, as well as with high electrical conductivity from maize residues [27]; (v) to obtain char with maximum yield and higher heating value from waste neem cake [4]; and (vi) to obtain chars with maximum calorific value and fixed carbon content from palm kernel shell

[28]. The pyrolysis parameters employed in these optimization studies vary from researcher to researcher. However, the most commonly employed include the following: temperature, residence time, heating rate, and nitrogen flow rate, with the latter reported to have insignificant/or minimal influence over the carbonization process, and consequently on the yield and quality of the resultant char [29, 30]. From the above discussions, it is evident that no optimization studies employing RSM have been conducted on rice husks, with a view to producing char with maximum yield, maximum fixed carbon content, as well as with minimum ash content.

Our previous study on characterization of rice husk varieties in Uganda revealed that upland rice husk varieties, and in particular New Rice for Africa (NERICA) 1, exhibits a reasonably lower ash content, as well as higher volatile matter and carbon contents, suiting it as a more potential precursor in numerous applications, for instance, in activated carbon production and biofuel production, than the other rice husk varieties in Uganda [10]. This study therefore aimed at optimizing pyrolysis conditions suited for production of char with maximum yield, maximum fixed carbon content, as well as with minimum ash content from Uganda's NERICA 1 rice husk variety, using RSM. Moreover, with such properties, a relatively higher surface area of the resultant char would be expected. The pyrolysis parameters included temperature, heating rate, and isothermal heating period. These were considered for optimization because of their important influence on the yield and quality of char. The optimized rice husk char was further characterized for elemental and proximate compositions, thermal behavior, specific surface area, as well as surface functional groups, in order to gain more insight into its quality, as a potential precursor for production of activated carbon.

2 Materials and methods

2.1 Sample collection and preparation

NERICA 1 rice variety was obtained from Buginyanya Zonal Agricultural Research and Development Institute (Bugi-ZARDI), Uganda. The rice grain was milled at a moisture content of 13–14% wet basis (wb) to obtain the rice husks. The husks were subsequently milled to fractions of particle size 250 μm , for subsequent char production, as well as for char characterization studies.

2.2 Char production and char yield

About 10–15 mg sample of the milled rice husk (particle size 250 μm) was placed in a platinum pan, and subsequently loaded into the furnace of the thermogravimetric analyzer (TA instruments Q500). The loaded sample was heated under N_2 flow (60 mL min^{-1}), with pyrolysis temperatures ranging from 400 to 600 $^{\circ}\text{C}$, heating rate 10–25 $^{\circ}\text{C min}^{-1}$, and

isothermal heating period 60–120 min. The generated rice husk char was subsequently cooled down to 30 °C, by purging the furnace with N₂ gas. Using the TA Universal analysis software, the char yield at the end of each experimental run was determined as the ratio of the oven dry sample weight at the end of pyrolysis to the weight of the dry raw sample.

2.3 Fixed carbon and ash contents

After the char was cooled down, as indicated in Sect. 2.2, and without necessarily having to offload the pan, the char was further subjected to thermogravimetric analysis (TGA) to determine its moisture content, volatile matter, ash, and fixed carbon contents. This was achieved by heating the still loaded char in the furnace of the thermogravimetric analyzer, from ambient temperature to 600 °C at a ramping rate of 20 °C min⁻¹ under nitrogen flow of 60 mL min⁻¹. At the same ramping rate, heating was continued up to 900 °C, but under air flow to allow for char oxidation. This temperature was held constant for 3 min until there was no further change in mass of the remaining residue. Using the TA Universal analysis software, the respective thermogravimetric curves of percent weight loss versus temperature were generated. From each of these, values of the moisture content, volatile matter, fixed carbon, and ash contents of char generated from each set of experimental conditions were read off. The moisture content was obtained as weight loss due to dehydration of rice husks from room temperature to temperatures ranging from 105 to 120 °C. Volatile matter content was obtained as weight loss due to thermal degradation between 120 and 600 °C. Fixed carbon content was obtained as the weight loss due to combustion of the remaining organic material at temperatures ranging from 600 to 900 °C. Lastly, the remaining residue after combustion of the organic material represented the ash content.

2.4 Design of experiments

The pyrolysis process parameters for char production were optimized using a standard RSM design, called central composite design (CCD). Temperature (A), heating rate (B), and isothermal heating period (C) were employed as the three input variables for a three-factor, two-level CCD. Table 1 shows the low and high levels of each factor denoted as -1 and +1, respectively.

Table 1 Experimental values used in CCD

Factor	Name	Units	Low (-1) value	High (+1) value
A	Temperature	°C	400	600
B	Heating rate	°Cmin ⁻¹	10	25
C	Isothermal heating period	Min	60	120

These three input variables together with their respective ranges were chosen based on both literature and the results obtained from our preliminary studies. Using Design-Expert software (version 11, Stat-Ease Inc., MN, USA), 20 experimental runs were planned in a randomized order to minimize the effects of the uncontrolled factors. The runs consisted of eight factorial points, six axial points, and six replicates at the center points as determined from Eq. (1). The center points were employed to determine the experimental error and the reproducibility of the data.

$$N = 2^n + 2n + n_c = 2^3 + 2(3) + 6 = 20 \quad (1)$$

where N is the total number of experiments required, n is the number of process variables, and n_c is the number of replicates at the center points.

2.5 Development of an empirical model

The responses that were optimized included the char yield, fixed carbon, as well as ash contents of the rice husk char. The mathematical relationship between the input variables and each of the responses was modeled using a polynomial Eq. (2).

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

where Y is the predicted response (either char yield, fixed carbon, or ash content), X_i and X_j are the independent variables (pyrolysis temperature, heating rate, and isothermal heating period), b_o 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.

The Design-Expert software was employed to obtain the regression models, as well as carry out the statistical analyses. The goodness of fit of the data to the developed models was evaluated based on values of the correlation coefficient (R^2), adjusted R^2 value, predicted R^2 value, adequate precision, and coefficient of variation (CV). Adequate precision was employed to measure the signal to noise ratio, while CV, which is the ratio of the standard error to the mean value of the observed response, was employed to determine the reproducibility of the models. From the ANOVA, Fisher's F test and probability (p value) were employed to confirm the statistical significance of the developed models, as well as the

regression coefficients (model terms), with 95% confidence level. The lack of fit F test was employed to evaluate the variations of the data around the fitted model, and its statistical significance was presented as probability of lack of fit (p -values of lack of fit). A backward selection with an alpha value of 0.10 was used to eliminate the insignificant model terms, which would otherwise increase the R^2 value, and consequently not indicate accurately the favorable regression model.

2.6 Optimization and model validation

From the Design-Expert software, the numerical optimization method was selected to optimize the pyrolysis process conditions. The targeted criteria was set to maximize each of the responses, while the values for each of the pyrolysis process parameters (temperature, heating rate, and isothermal heating period) were set to the ranges being studied. Design-Expert software then searches for a combination of factors that simultaneously satisfy the requirements placed on each of the response and factors. The developed response surface models were validated by conducting the respective experiments under the obtained optimum pyrolysis conditions. The experimental values obtained were then compared with the values predicted by the model.

2.7 Char characterization

2.7.1 Elemental composition and specific surface area

The elemental composition of the optimized rice husk char involved determining its carbon, hydrogen, and sulfur contents using an ELTRA CHS analyzer. The specific surface area of the optimized rice husk char was determined by liquid nitrogen at 77 K, using an automatic adsorption instrument (BELSORP-mini, BEL Japan, Inc.), based on the Brunauer, Emmett, and Teller (BET) method [31]. However, prior to measurement, about 100–120 mg sample of the activated carbon was adequately pretreated, first by oven drying overnight at 105 °C and later degassing under vacuum in the sorption analyzer at 300 °C under N_2 atmosphere for 3 h.

2.7.2 Thermal behavior

The thermal behavior of the optimized rice husk char was studied by subjecting the char to TGA in an inert N_2 atmosphere. This involved heating about 10–15 mg of the char sample in the furnace of thermal analyzer (TA instruments Q500) from ambient temperature (25 °C) to 600 °C, at a heating rate of 20 °C min^{-1} , and N_2 flow (50 mL min^{-1}). Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of percent weight loss (%wt) versus temperature (°C) and percent rate of weight loss (%wt min^{-1}) versus

temperature (°C), respectively, were generated using TA universal software.

2.7.3 Functional properties

Identification of surface functional groups in the optimized rice husk char was done by employing the Fourier transform infrared (FTIR)-attenuated total reflection (ATR) spectroscopy (model TENSOR27, Bruker, Germany). The spectra were obtained by scanning in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} . The spectra were recorded after clamping the sample on the probe. The background scan was obtained using a diamond crystal for each experimental condition.

3 Results and discussion

3.1 Development of regression model equations

CCD was employed to develop correlations between the pyrolysis process variables (pyrolysis temperature, heating rate, and isothermal heating period) and the responses (char yield, fixed carbon, and ash contents). The experimental design, together with corresponding experimental values for each of the responses, is shown in Table 2.

Runs 2, 3, 4, 6, 14, and 19 at the center point were employed to determine the experimental error and the reproducibility of the data. As can be seen from Table 2, char yields, fixed carbon, as well as ash contents ranged 30–39%db, 52–60%db, and 31–43%db, respectively. These relatively wide ranges are attributed to the different extents to which rice husk biomass was devolatilized at the various pyrolysis conditions [32].

In order to find the best fit for each of the responses, the respective sequential model sum of squares was considered. From each of these, the highest order polynomial, where the additional terms are significant, and the model is not aliased, was chosen. In this study, the quadratic model was found to best fit the responses, as suggested by the Design-Expert software. In terms of coded factors, the response surface reduced quadratic models corresponding to char yield (Y_1), fixed carbon content (Y_2), and ash content (Y_3), after excluding the insignificant terms are given in Eqs. (3)–(5), respectively.

$$Y_1 = 32.47 - 2.22A - 0.8828C + 0.8145A^2 \quad (3)$$

$$Y_2 = 57.72 + 1.21A - 0.7204C - 0.85AC - 1.03A^2 \quad (4)$$

$$Y_3 = 39.44 + 2.70A - 0.0535B + 0.6930C - 0.5550BC - 1.31A^2 \quad (5)$$

where A is the temperature (°C), B is the heating rate (°C min^{-1}), and C is the isothermal heating period (min).

Table 2 CCD and the experimental results

Run	Pyrolysis conditions			Responses		
	A (temperature, °C)	B (heating rate, °C min ⁻¹)	C (heating period, minute)	Y ₁ (char yield, %db)	Y ₂ (fixed carbon content (%db))	Y ₃ (ash content (%db))
1	400.00	25.00	120.00	34.44	55.86	35.23
2	500.00	17.50	90.00	31.91	57.00	40.26
3	500.00	17.50	90.00	31.89	57.52	39.72
4	500.00	17.50	90.00	31.59	56.80	40.34
5	400.00	10.00	60.00	35.35	54.45	35.41
6	500.00	17.50	90.00	32.39	57.52	39.79
7	600.00	10.00	60.00	32.52	59.51	38.98
8	400.00	25.00	60.00	37.11	55.94	34.90
9	600.00	25.00	60.00	31.83	58.25	40.63
10	600.00	25.00	120.00	30.60	57.03	39.60
11	400.00	10.00	120.00	34.67	55.92	35.68
12	600.00	10.00	120.00	30.24	55.32	42.45
13	500.00	17.50	39.55	34.38	59.82	37.40
14	500.00	17.50	90.00	32.00	57.41	39.96
15	500.00	30.11	90.00	32.59	58.26	39.28
16	500.00	4.89	90.00	33.55	59.13	38.43
17	668.18	17.50	90.00	30.54	57.58	41.01
18	500.00	17.50	140.45	31.29	56.36	41.22
19	500.00	17.50	90.00	32.84	58.17	39.37
20	331.82	17.50	90.00	38.85	52.50	31.21

3.2 Analysis of variance

ANOVA was employed to evaluate the statistical significance of the quadratic models, their lack of fits, as well as the statistical significance of their respective model coefficients. As can be seen from Table 3, the model F values of 81.29, 18.50, and 38.33 corresponding to the reduced quadratic models for char yield, fixed carbon, and ash contents, respectively, imply that the developed models are significant (p values < 0.05). For each of the developed models, there is only a 0.01% chance that a model F value this large could occur due to noise. Besides, the lack of fits for the developed models is not significant (p value > 0.05), further suggesting that the quadratic models adequately describe the functional relationship between the experimental factors and the response variables.

Based on the fact that model terms are significant for p -values less than 0.05, and that model terms are not significant for p values greater than 0.10, then A , C , and A^2 are the significant terms for the response surface reduced quadratic model for char yield (Table 3). Out of these, temperature (F value 187.29) was found to be the most significant factor influencing char yield, followed by the isothermal heating period (F value 29.55), and lastly the quadratic effect of temperature (F value 27.02). The main effect of heating rate, together with the interactive effects between the pyrolysis parameters, were

found not to have significant influence on char yield, since their p values were greater than 0.05. Similar findings were reported by [25], possibly due to the relatively similar chemical compositions of the rice husk biomass employed in the different studies. The findings in this study are also in agreement with previous studies which revealed that (i) once lignocellulosic materials are pyrolyzed at temperatures beyond 300 °C, then heating rate does not significantly influence their char yields [15]; and (ii) the effect of heating rate on char yield resulting from pyrolysis of biomass to the same final temperature is at most minor [33].

The significant terms for the response surface reduced quadratic model corresponding to fixed carbon content include A , C , AC , and A^2 (Table 3). Out of these, the main effect of temperature (F value 30.54) was found to have the most significant influence on the fixed carbon content of the rice husk char, followed by the quadratic effect of temperature (F value 23.68), isothermal heating period (F value 10.88), and lastly the interactive effect between temperature and the isothermal heating period (F value 8.87). A , C , BC , and A^2 are the significant terms for the response surface reduced quadratic model for ash content (Table 3). Out of these, temperature (F value 142.67) was found to be the most significant factor influencing ash content, followed by the quadratic effect of temperature (F value 36.03), isothermal heating period (F value 9.37),

Table 3 ANOVA for response surface reduced quadratic models for char yield (a), fixed carbon (b), and ash contents (c)

Source	Sum of squares	df	Mean square	F value	p value Prob > F	Remarks
(a) ANOVA for response surface reduced quadratic models for char yield						
Model	87.85	3	29.28	81.29	< 0.0001	Significant
A-Temperature	67.47	1	67.47	187.29	< 0.0001	Significant
C-Isothermal heating period	10.64	1	10.64	29.55	< 0.0001	Significant
A ²	9.74	1	9.74	27.02	< 0.0001	Significant
Residual	5.76	16	0.3603			
Lack of fit	4.78	11	0.4348	2.21	0.1962	Not significant
Pure error	0.9819	5	0.1964			
Cor total	93.62	19				
(b) ANOVA for response surface reduced quadratic models for fixed carbon content						
Model	48.19	4	12.05	18.50	< 0.0001	Significant
A-Temperature	19.90	1	19.90	30.54	< 0.0001	Significant
C-Isothermal heating period	7.09	1	7.09	10.88	0.0049	Significant
AC	5.78	1	5.78	8.87	0.0094	Significant
A ²	15.43	1	15.43	23.68	0.0002	Significant
Residual	9.77	15	0.6514			
Lack of fit	8.63	10	0.8629	3.78	0.0776	Not significant
Pure error	1.14	5	0.2283			
Cor total	57.96	19				
(c) ANOVA for response surface reduced quadratic models for ash content						
Model	134.09	5	26.82	38.33	< 0.0001	Significant
A-Temperature	99.82	1	99.82	142.67	< 0.0001	Significant
B-Heating rate	0.0391	1	0.0391	0.0558	0.8166	Not significant
C-Isothermal heating period	6.56	1	6.56	9.37	0.0084	Significant
BC	2.46	1	2.46	3.52	0.0816	Significant
A ²	25.21	1	25.21	36.03	< 0.0001	Significant
Residual	9.79	14	0.6996			
Lack of fit	9.14	9	1.02	7.79	0.0180	Not significant
Pure error	0.6519	5	0.1304			
Cor total	143.89	19				

and lastly, the interactive effect of heating rate and heating period (F value 3.52). Similar tendencies were observed during biochar production from maize residues [27], possibly due to similarity in the chemical composition of the different biomass.

The goodness of fit of the data to the developed models was evaluated based on the standard deviation, coefficient of variation, R^2 value, adjusted R^2 value, predicted R^2 value, and adequate precision (Table 4). The standard deviation corresponding to each of the responses was small, indicating that the developed models are good. The values of coefficient of variation for the respective responses were less than 10, suggesting good reproducibility of the developed models [34]. The high R^2 values indicate that the data satisfactorily fits the developed models. More specifically, 93.84, 83.14, and 93.19% of the fitnesses in the responses of char yield, fixed carbon, and ash contents,

respectively, can be explained by the respective models in Eqs. (3), (4), and (5), respectively. Moreover, the adjusted and predicted R^2 values corresponding to each of the responses were in

Table 4 Model summary statistics indicating goodness of fit of the developed models

Statistical parameter	Char yield	Fixed carbon	Ash content
Standard deviation	0.6002	0.8071	0.8364
Mean	33.03	57.02	38.54
Coefficient of variation (%)	1.82	1.42	2.17
R^2 value	0.9384	0.8314	0.9319
Adjusted R^2 value	0.9269	0.7865	0.9076
Predicted R^2 value	0.8994	0.6669	0.8354
Adequate precision	31.0440	16.5582	23.8973

reasonable agreement, since their difference was less than 0.2 (Table 4), confirming the favorability of the developed models. Since adequate precisions (signal to noise ratio) were found greater than 4, then the respective developed models can be employed to navigate the design space.

3.3 Diagnostics and adequacy checking

The adequacy of the fitted models was checked, to ascertain their validity. For a good model, the residuals should be randomly and normally distributed. To ascertain this, normal probability plots of the internally studentized residuals, the predicted versus actual values of the responses, as well as plots of externally studentized residuals versus predicted values were used. Figure 1a–c shows that the points on the normal probability plots conform to a straight line, confirming normal distribution of the data.

The plots of predicted versus actual values of char yield and fixed carbon content shown in Fig. 1d–f, respectively,

show minimal divergence of points from the straight line. Consequently, the respective response surface models developed can be used to adequately represent the functional relationship between the experimental factors and the response variables.

The plots of externally studentized residuals versus predicted values for char yield (Fig. 2a), fixed carbon (Fig. 2b), and ash content (Fig. 2c) do not show any particular pattern, suggesting random distribution of the residues—a requirement of a good model.

3.4 Response surfaces

3.4.1 Char yield

Figure 3a–c shows the three-dimensional response surfaces that were plotted to show the effects between the pyrolysis variables on the resulting char yield. From the plots, it can noticeably be seen that the interactive effect between the

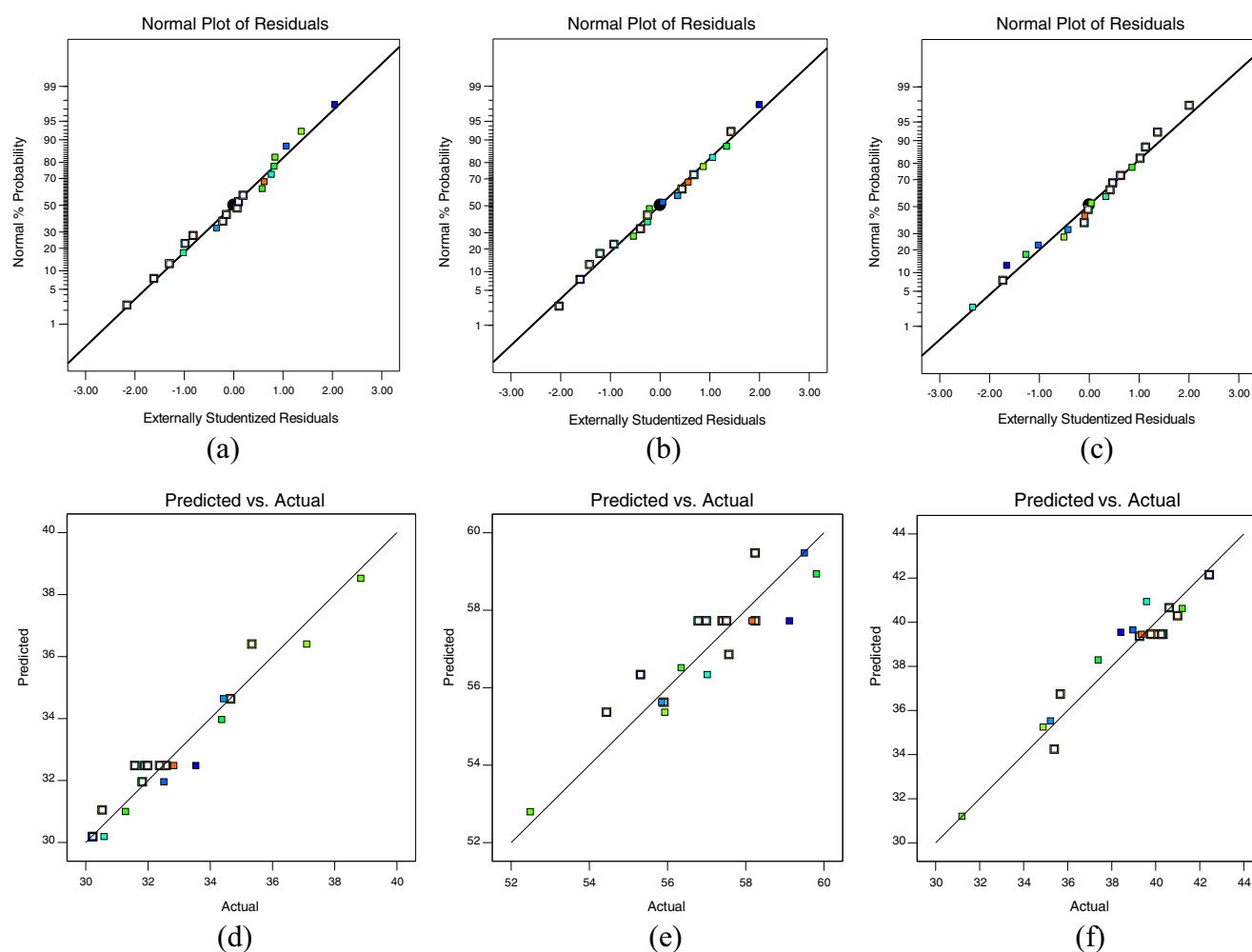


Fig. 1 Normal probability plot of residues for **a** char yield, **b** fixed carbon content, and **c** ash content; predicted values versus experimental values for **d** char yield, **e** fixed carbon content, and **f** ash content

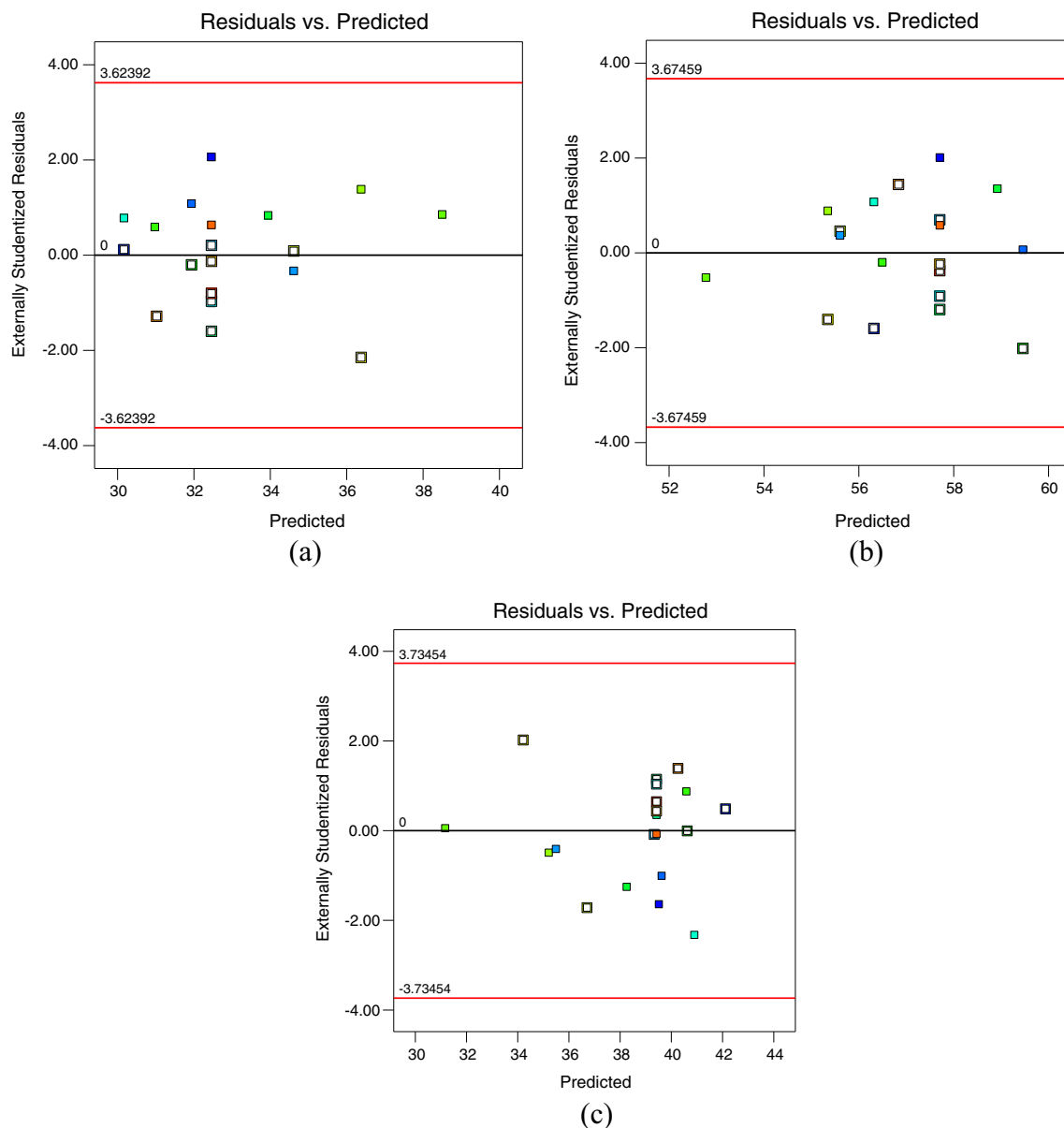


Fig. 2 Residues versus predicted for **a** char yield, **b** fixed carbon content, and **c** ash content

pyrolysis temperature and isothermal heating period (Fig. 3a) had the greatest influence on char yield, followed by the interactive effect between pyrolysis temperature and heating rate (Fig. 3b), and lastly, the interactive effect between the isothermal heating period and heating rate (Fig. 3c). At the same heating rate and isothermal heating period, the char yield decreased with increasing pyrolysis temperature. This may be attributed to the large amounts of volatiles released, due to greater primary decomposition of the rice husks, and/or due to secondary decomposition of the char [19]. Similarly, at the same pyrolysis temperature and heating rate (Fig. 3c), the char yield decreased with increase in isothermal heating period. This is possibly due to the enhanced effect of heat and mass transfer, leading to further pyrolysis, and consequently

more devolatilization of the rice husk material [35]. However, most of the volatiles were most probably released during the first 60 min, such that any further increase in the isothermal heating period, resulted in only a slight decrease in char yield (see Fig. 3a, c). Similar tendencies were observed, when oil palm kernel shell was pyrolyzed at temperatures ranging from 600 to 700 °C, for an isothermal heating period of 60–240 min [36].

From Fig. 3b, c, it can noticeably be seen that heating rate had less influence on char yield. Similar tendencies have been reported by [25]. From the discussions above, it is evident that higher char yields could be obtained by pyrolyzing rice husks at relatively lower pyrolysis temperatures, and for shorter isothermal heating periods.

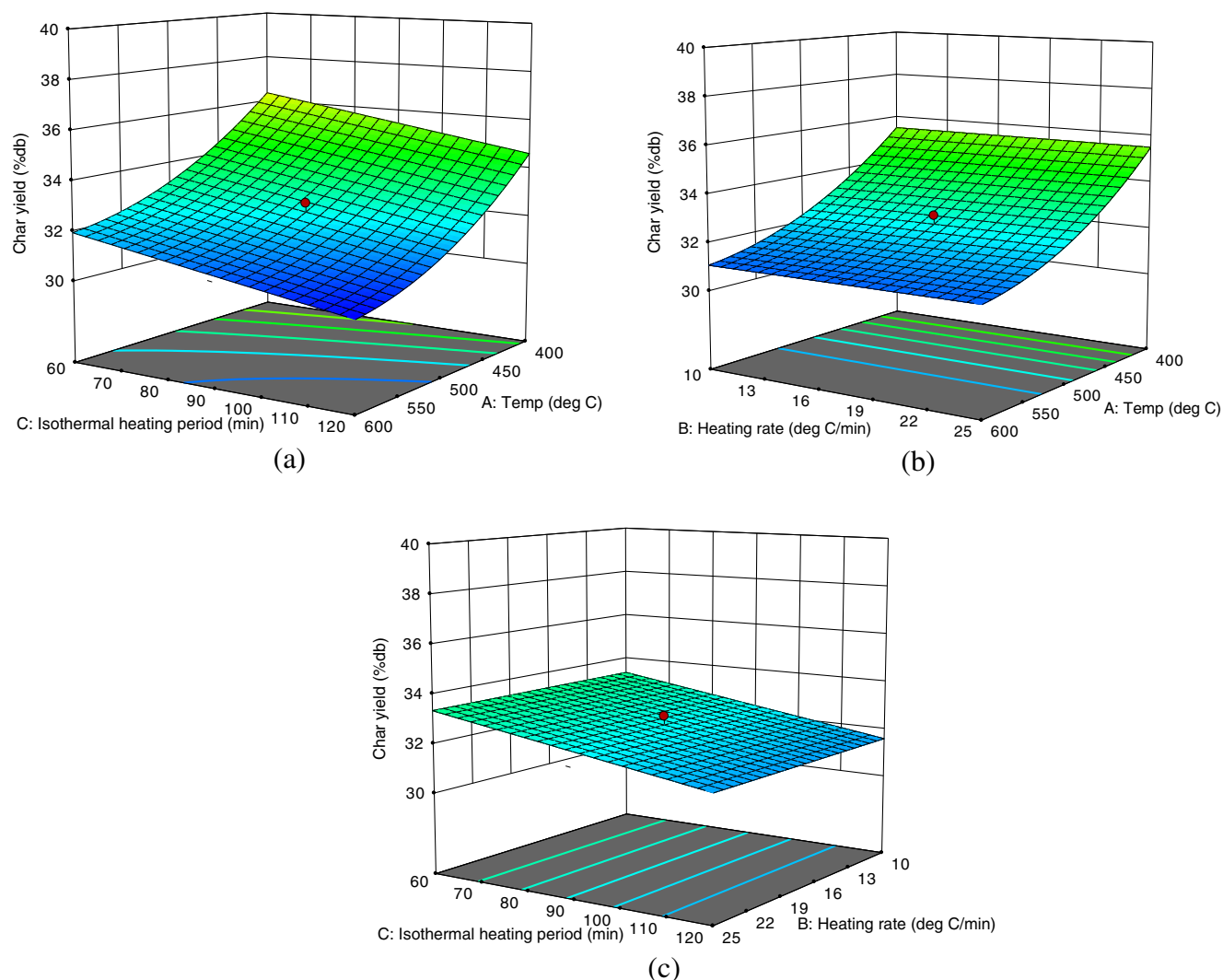


Fig. 3 Three-dimensional response surface plots of char yield. **a** Effect of pyrolysis temperature, isothermal heating period, and heating rate fixed at $17.5\text{ }^{\circ}\text{C min}^{-1}$. **b** Effect of pyrolysis temperature, heating rate, and

isothermal heating period fixed at 90 min. **c** Effect of isothermal heating period, heating rate, and pyrolysis temperature fixed at $500\text{ }^{\circ}\text{C}$

3.4.2 Fixed carbon content

Figure 4a–c shows the three-dimensional response surfaces that were plotted to show the interactive effects between the pyrolysis variables on the fixed carbon content of the resulting rice husk char. From the plots, it can noticeably be seen that the interactive effect between pyrolysis temperature and isothermal heating period had the greatest influence on the fixed carbon content (Fig. 4a), followed by the interactive effect between pyrolysis temperature and heating rate (Fig. 4b), and lastly the interactive effect between isothermal heating period, and heating rate (Fig. 4c).

At the same heating rate and isothermal heating period, the increase in fixed carbon content with increase in pyrolysis temperature may be attributed to the increased devolatilization of the biomass during pyrolysis, where the more reactive oxygen and hydrogen are majorly removed, leaving behind a

higher fixed carbon content in the char [37, 38]. On the contrary, a study by Alvarez [39] found the fixed carbon content of the rice husk char to decrease with increasing pyrolysis temperature, which was presumably attributed to the increased concentration of ash in the resultant char. Such contrasting results possibly suggest that the overall effect of pyrolysis temperature on the fixed carbon content may vary with biomass type, reactor type, and/or the pyrolysis conditions employed. On the other hand, at the same pyrolysis temperature and heating rate, the fixed carbon content of char decreased slightly with increasing isothermal heating period (see Fig. 4a, c). This suggests that pyrolysis of rice husks for prolonged retention times could have a negative influence on the fixed carbon content of the resulting char. Similar tendencies were observed in a study by [25], where pyrolysis parameters were optimized to produce char with maximum total organic carbon from empty fruit palm bunches. On the

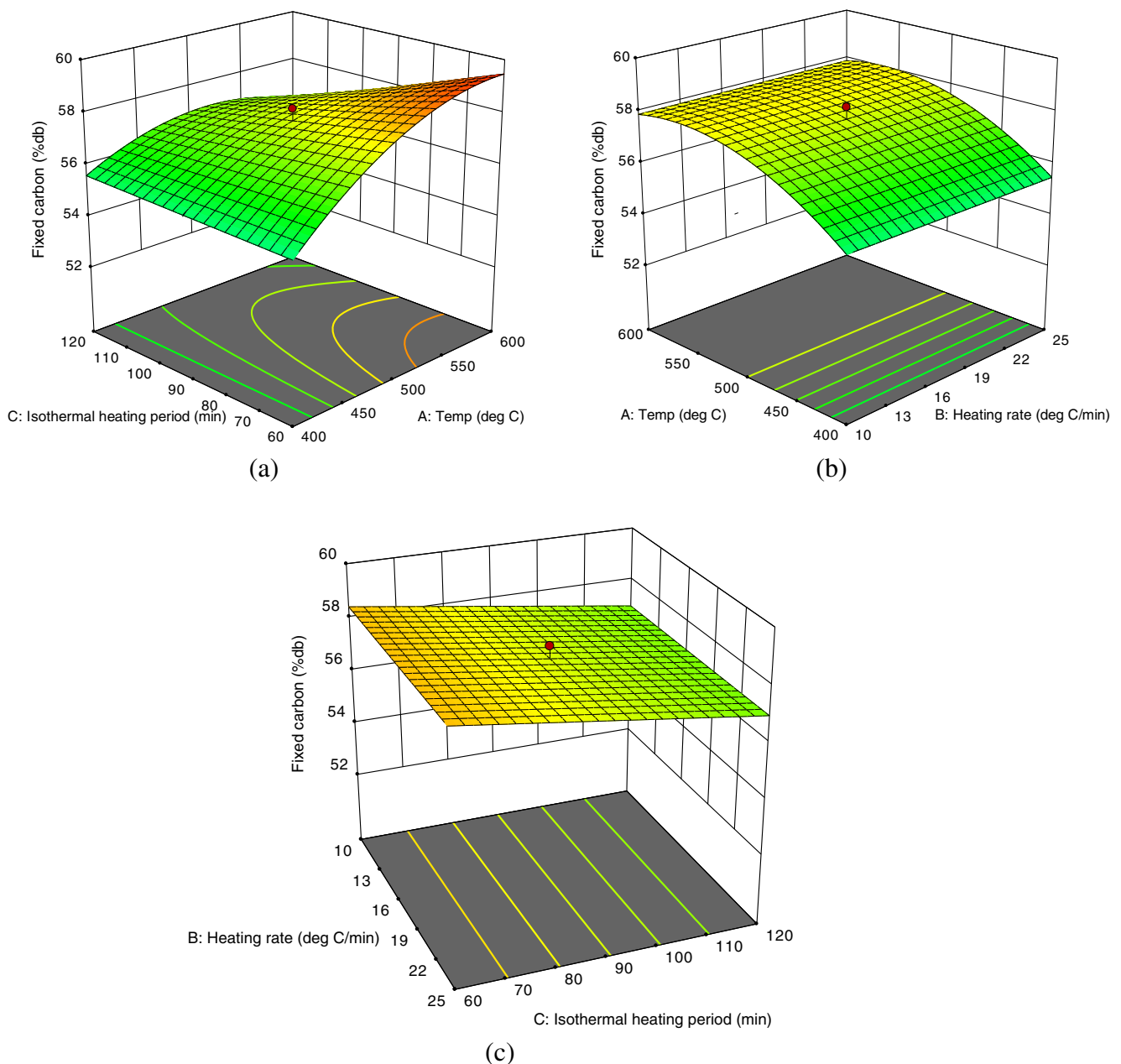


Fig. 4 Three-dimensional response surface plots of fixed carbon content. **a** Effect of pyrolysis temperature, isothermal heating period, and heating rate fixed at $17.5\text{ }^{\circ}\text{C min}^{-1}$. **b** Effect of pyrolysis temperature, heating

rate, and isothermal heating period fixed at 90 min . **c** Effect of isothermal heating period, heating rate, and pyrolysis temperature fixed at $500\text{ }^{\circ}\text{C}$

contrary, the same authors found the prolonged retention time to have a positive influence on the total organic carbon content of char produced from the pyrolysis of rice husks. They attributed these differences to the structural characteristics of the biomass which makes it susceptible to destruction. As can be seen from Fig. 4b, c, the effect of heating rate did not have considerable influence on the fixed carbon content of the resulting rice husk char. However, elsewhere, the carbon content of rice husk char was found to increase with decreasing heating rate [25]. From the above plots, it can be stated that pyrolysis of rice husks at higher pyrolysis temperatures,

coupled with shorter isothermal heating periods, results in higher fixed carbon content of the resulting char.

3.4.3 Ash content

Figure 5a–c shows the three-dimensional response surfaces that were plotted to show the interactive effects between the pyrolysis variables on the ash content of the resulting rice husk char. From the plots, it can noticeably be seen that the interactive effect between pyrolysis temperature and isothermal heating period (Fig. 5a), as well as the interactive effect

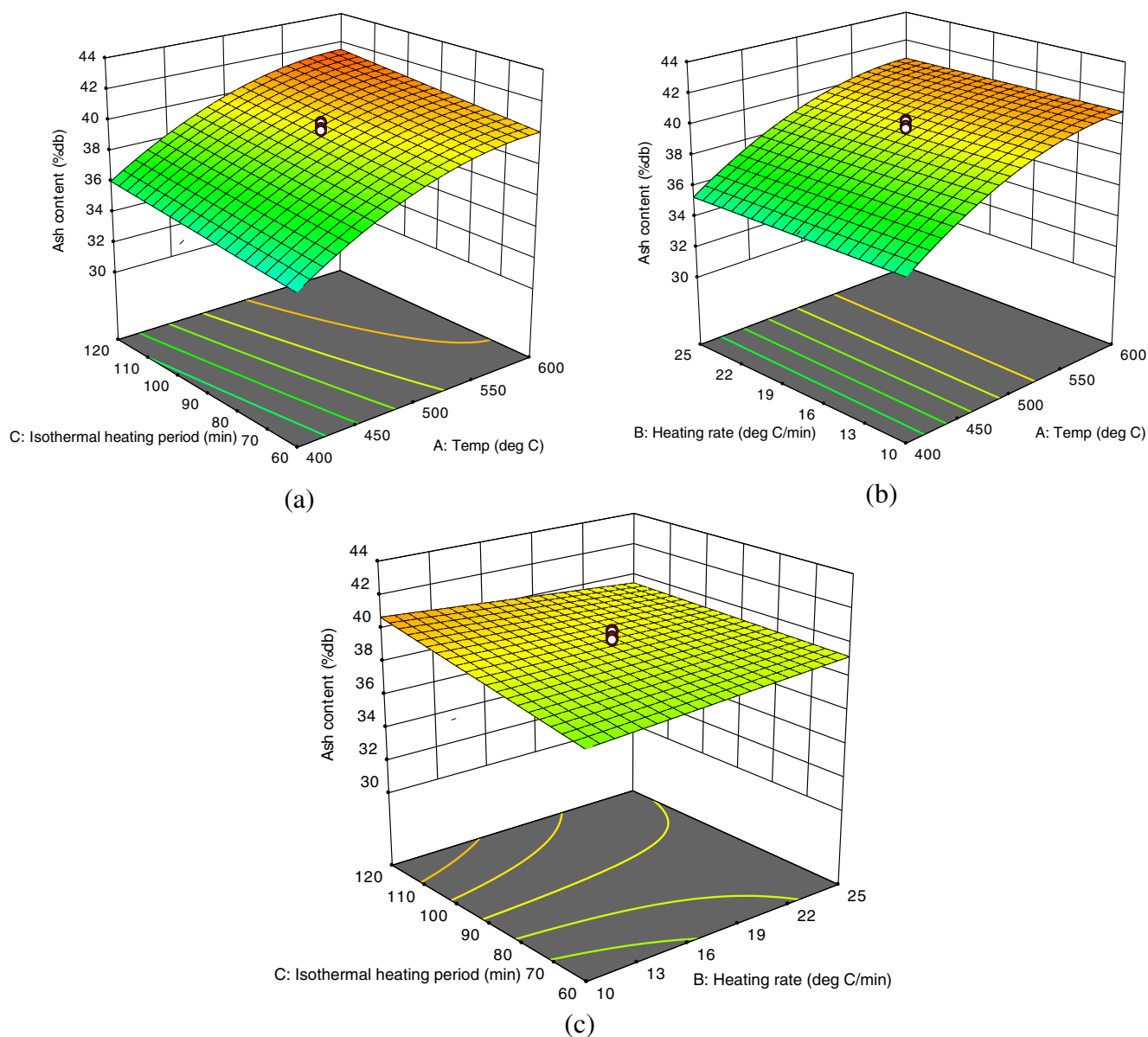


Fig. 5 Three-dimensional response surface plots of ash content. **a** Effect of pyrolysis temperature, isothermal heating period, and heating rate fixed at $17.5\text{ }^{\circ}\text{C min}^{-1}$. **b** Effect of pyrolysis temperature, heating rate, and

isothermal heating period fixed at 90 min . **c** Effect of isothermal heating period, heating rate, and pyrolysis temperature fixed at $500\text{ }^{\circ}\text{C}$

between pyrolysis temperature and heating rate (Fig. 5b), had the greatest influence on the ash content of the resulting rice husk char. In all these scenarios, the ash content of the rice husk char considerably increased with increase in pyrolysis temperature, and to a lesser extent with increase in isothermal heating period. This increase may be attributed to the volatilization of elements such as C, H, N, O, and S, leaving behind a higher concentration of the typically less volatile ash (inorganics) in the char [40]. The interactive effect between the isothermal heating period and heating rate did not have much influence on the ash content of the resulting rice husk char (Fig. 5c). From these discussions, it can be stated that to obtain rice husk char with a relatively lower ash content,

suiting it as activated carbon precursor, rice husk could be pyrolyzed at relatively lower pyrolysis temperatures, as well as at lower isothermal heating periods.

3.5 Process optimization and validation

After model simulation using the numerical optimization method of the Design-Expert software, the optimum pyrolysis conditions were suggested as follows: pyrolysis temperature ($406\text{ }^{\circ}\text{C}$), heating rate ($10\text{ }^{\circ}\text{C min}^{-1}$), and isothermal heating period (60 min). If rice husks were pyrolyzed at these conditions, the char yield, fixed carbon, and ash content as predicted by the respective developed models are $36.17\%\text{db}$, $55.59\%\text{db}$,

and 34.54%db, respectively (Table 5). To verify the predictive capability of the developed models, the rice husk char was prepared under the suggested optimum pyrolysis conditions, assessed for char yield, fixed carbon, as well as ash content, and subsequently their values compared with the predicted values. As a rule of thumb, the mean experimental values should 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, or else 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 (Table 5), suggesting that the developed models are valid.

The deviations between the actual and the predicted values were considerably small, with only 2.58, 0.38, and 1.34%, for char yield, fixed carbon, and ash contents, respectively, further confirming the good agreement between the experimental and predicted values. However, since the thermogravimetric unit employed in this study to produce char was of a laboratory scale, the obtained models, and consequently the optimization results, may not necessarily extrapolate well to the relatively larger scale pyrolysis reactors. Moreover, in an attempt to ascertain the limitations of extrapolation, and consequently the limitations of the optimization results, pyrolysis experiments to produce char were performed in a relatively larger tube furnace, where the obtained optimal conditions were employed, and the proximate composition of the resultant rice husk char subsequently determined via TGA. The char yield, fixed carbon, and ash contents of the resultant rice husk char were obtained as 34.68, 57.24, and 32.60%db, respectively. As can be seen from Table 5, these results compare quite well with those of the char obtained by pyrolysis of the rice husk in a thermogravimetric unit.

3.6 Char characterization

3.6.1 Proximate and elemental compositions

Table 6 shows the specific surface area, proximate and elemental compositions of the raw rice husks, as well as of the optimized rice husk char. For purposes of comparison, the compositions of other rice husk chars, as well as of other biomass-derived chars from the literature have been included in Table 6. The results vary from researcher to researcher,

possibly due to differences in the biomass properties, reactor type, as well as due to differences in the pyrolysis conditions employed in the different studies. For instance, the relatively higher char yield obtained in this study, as compared to those obtained from the fast pyrolysis of rice husk by Alvarez [39, 41] was expected. Essentially, slow pyrolysis which was typically employed in this study involves slow heating of the biomass for longer residence times in the reactor, promoting secondary reactions of the pyrolysis vapors, which consequently lead to greater char formation [42]. On the other hand, fast pyrolysis involves rapid heating of the biomass for shorter residence times in the reactor, minimizing secondary reactions in the reactor, and consequently leading to higher bio-oil yields [43]. It can also be seen from Table 6 that the resultant char exhibited a lower surface area, as compared to those reported in the literature [25, 26, 32, 40]. The lower surface area could be compensated for by the higher char yield, which enhances the economic viability of the pyrolysis process. Besides, the relatively lower pyrolysis temperature employed in this study suggests lower energy requirements, further enhancing the economic viability of the pyrolysis process.

Compared to the composition of the raw rice husks employed in this study, the carbon and ash contents of the resulting rice husk char at 406 °C substantially increased, while its hydrogen content decreased, for reasons already cited in Sects. 3.4.2 and 3.4.3. The enrichment in carbon content suggests good prospects for utilizing the produced rice husk char as activated carbon precursor. This is because a high carbon content subsequently leads to a high carbon yield, while at the same time, activated carbon with good adsorptive properties could be produced, once the rice husk char is activated. However, the increased ash content in the rice husk char could be a hindrance to its application as an activated carbon precursor, since ash obstructs pore formation, leading to activated carbon with low adsorption capacity [44]. Therefore, in an attempt to lower the ash content of the rice husk char, and consequently enhance its properties suited for an activated carbon precursor, the rice husk char may be alkaline pretreated with compounds, such as sodium hydroxide [41, 45]. The alkaline pretreatment step may also be carried out on the raw rice husk, prior to pyrolysis [46]. The sodium silicate thus formed can be converted to silica, by addition of suitable amounts of mineral acid, thus enhancing the economic feasibility of the pyrolysis process [47]. Silica recovery as high as

Table 5 Validation experiments for the proposed models

	Model for the char yield (%db)	Model for the fixed carbon content (%db)	Model for the ash content (%db)
95% PI low	35.25	54.22	33.02
95% PI high	37.09	56.97	36.04
Mean experimental value	35.26	55.39	35.01
Predicted value	36.17	55.60	34.54

Table 6 Specific surface area, elemental and proximate compositions of the raw rice husk, as well as optimized rice husk char, as compared to char produced elsewhere

Biomass type	Pyrolysis temp (°C)	Specific surface area (m ² g ⁻¹)	Proximate composition (%db)			Elemental composition (%daf)				Char yield (%db)	Reference
			Volatile matter	Ash	Fixed carbon	C	H	S	Others		
Raw rice husk*	NA	1.58	67.06	13.80	19.14	37.30	6.30	0.23	56.17	NA	[10]
Rice husk char	406	123.88	9.60	35.01	55.39	60.35	3.99	0.60	35.06	35.26	This study
Rice husk char	500	230.91	—	—	—	44.64	3.96	0.02	—	34.63	[40]
Oil palm fiber char	—	158.00	38.45	6.60	54.94	60.37	3.21	0.71	35.71	36.79	[26]
Rice husk char	600	397.00	—	61.33	—	87.38	1.22	0.02	11.38	31.70	[32]
Rice husk char	700	202.12	—	—	—	—	—	—	—	—	[25]
Rice husk char	500	25.60	12.80	51.30	36.00	45.20	1.50	—	53.30	26.00	[41]

*NERICA 1 rice husk variety employed in this study

%daf %dry-ash-free basis, NA not applicable

88 wt% from rice husk char have been reported [41]. With such promising results, the possibility of silica recovery from rice husk varieties in Uganda and/or from the resultant char could be explored in future studies, with a view of enhancing the economic viability of the pyrolysis process.

3.6.2 Thermal behavior

The thermal behavior of the raw rice husk, as well as of the rice husk char, is depicted in the TG/DTG curves (Fig. 6a). These curves indicate that thermal degradation of raw rice husk occurs in three temperature zones, with the first temperature zone commencing at room temperature up to about 125 °C. Within this zone, a weight loss (5.67 wt%) occurred, due to dehydration of the rice husk material. This zone further extended up to about 206.0 °C, but with very slight weight loss, which could be attributed to loss of light volatiles from the rice husk material. This slight weight loss also suggests

that the organic constituents in the rice husk material are still thermally stable within this temperature zone. The second temperature zone (206.0–383.0 °C) was characterized by a major weight loss (58.7 wt%). More specifically, thermal degradation in this zone occurred via two reaction steps, distinguishable by two overlapping DTG peaks. The first peak (312.4 °C) corresponding to the lower temperature shoulder on the left of the DTG curve represents thermal degradation of hemicellulose within the material, while the higher temperature peak (347.1 °C) represents thermal degradation of cellulose [48]. Thermal degradation of raw rice husk in the third temperature zone (383.0–800 °C) occurred with a relatively small weight loss (10.8 wt%). This zone is represented by a flat trailing section, which is attributed to the slow decomposition of lignin over a wide temperature range, which even overlaps with that of cellulose and hemicellulose [49]. Consequently, a distinct weight loss derivative peak was not obvious for thermal degradation of lignin.

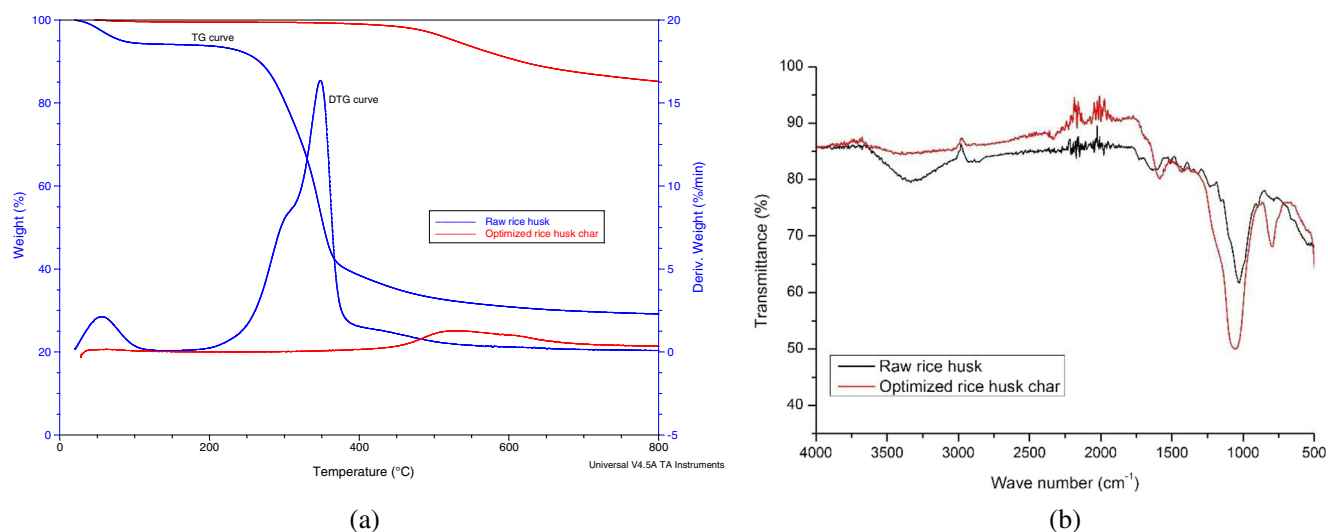


Fig. 6 TG and DTG curves of raw rice husk and rice husk char generated at 406 °C, 10 °C min⁻¹, and 60 min (a). FTIR spectra of the raw rice husk and optimized rice husk char (406 °C, 10 °C min⁻¹ and 60 min) (b)

The rice husk char was thermally stable right from room temperature to about 400 °C, where only 0.97 wt% of the total char weight was lost. The disappearance of characteristic peaks on the DTG curve of the rice husk char suggests that both the hemicellulose and cellulose components were possibly decomposed, upon pyrolysis of the rice husks. Majority of these components are lost as volatiles, while the remaining small fraction contributes to char formation [50]. Because of the decomposition of these components, a microporous rice husk char could be obtained, suiting it as a more potential precursor in the production of activated carbon, and other value-added products. Beyond 400 °C, the rice husk char experienced a slight weight loss (13.92 wt%), due to its greater decomposition at higher pyrolysis temperatures. From the above discussions, it is evident that a major fraction of the volatiles was lost when rice husks were pyrolyzed at the optimal conditions obtained in this study. However, to completely devolatilize the rice husk char, and possibly form a more porous activated carbon, thermal activation of the rice husk char could be carried out at activation temperatures much higher than 400 °C.

3.6.3 Surface functional groups

The FTIR spectra of the raw rice husk, as well as of the optimized rice husk char, are shown in Fig. 6b. The peak around 3335 cm^{-1} exhibited by the raw rice husk may be attributed to the –OH stretching vibrations from either alcohols found in cellulose, hemicellulose, lignin, extractives, carboxylic acids, silanol group (Si–OH), or from the water adsorbed by the rice husk [51]. This peak was less intensified in the optimized rice husk char, possibly due to dehydration of the char during its formation via pyrolysis [52].

The peak around 2932 cm^{-1} exhibited by the raw rice husk is typical of aliphatic C–H stretching of the hemicellulose and cellulose components [53], while the peak around 1725.78 cm^{-1} may be attributed to C=O vibration of the esters, ketones, and aldehydes in hemicellulose [54]. The disappearance of these peaks in the optimized rice husk char suggests that both the hemicellulose and cellulose components in the rice husk were thermally decomposed at the pyrolysis temperature of 406 °C. This confirms our findings on the thermal behavior of the rice husk char, indicated in Sect. 3.6.2. Assignment of functional groups to the less prominent bands around 2325–1879 cm^{-1} could not be unambiguously done. The peak around 1603.21 cm^{-1} exhibited by the raw rice husk may be attributed to the carbon–carbon double bond (C=C) stretching vibration of lignin [55]. This peak shifted to 1584.57 cm^{-1} upon pyrolysis of the rice husk. The strong peaks around 1034 and 810 cm^{-1} exhibited by the raw rice husk may be attributed to O–Si–O stretching, suggesting presence of silica in the raw rice husk [56]. These peaks shifted to wave numbers of 1053.61 and 793.25 cm^{-1} , respectively, as

shown in the FTIR spectra of the optimized rice husk char. Moreover, the peaks were more intensified, compared to those of the raw rice husk, possibly due to the increased concentration of ash (predominantly silica) in the char, upon devolatilization of the rice husk at 406 °C. However, further analyses of the rice husks and of the resultant char by X-ray fluorescence (XRF) may be required, to confirm the presence of silica and any other constituent elements.

4 Conclusions

RSM was employed to optimize pyrolysis conditions for production of char best suited as activated carbon precursor from Uganda's New Rice for Africa (NERICA) 1 rice husk variety. Pyrolysis temperature was found to exhibit the greatest influence over char yield, fixed carbon, as well as ash content, followed by heating period, and lastly heating rate. Optimum pyrolysis conditions were found to be 406 °C, 10 °C min^{-1} , and 60 min, resulting in char yield, fixed carbon, and ash contents of 35.26, 55.39, and 35.01%db, respectively. These results compare quite well with those of the char obtained by pyrolysis of the rice husk in a relatively larger tube furnace, operated under similar pyrolysis conditions, suggesting that the optimization results could be extrapolated to the tube furnace. Compared to raw rice husk, the resulting char was found more suited as activated carbon precursor, due to its enriched carbon content, and specific surface area. Thermal activation temperatures higher than 400 °C may be required to considerably devolatilize the char, forming a more porous activated carbon.

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Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

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