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Pyrolysis of sandbox (*Hura crepitans*) shell: Effect of pyrolysis parameters on biochar yield

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Abstract

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Pyrolysis of sandbox shell was carried out with the aim of investigating the effect of pyrolysis parameters on the pyrolysis process and identifies production conditions for the yield of biochar. Parameters investigated were heating temperature (400, 500 and 600°C), heating time (10, 20, and 30 min) and particle size of feedstock (0–1.0, 1.0–2.5 and 2.5–5.0 mm) in a laboratory batch pyrolysis process. The experiment was designed by applying response surface methodology through a three-factor full factorial design. The quadratic polynomial model obtained explains adequately the modelled response with coefficient of correlation, R^2 value of 0.8698. All the three variables significantly affected the biochar yield from sandbox shell, with heating temperature being the most effective followed by heating time and particle size of feedstock. Maximum biochar yield of 39.65% wt. occurred at 400°C heating temperature and 10 min heating time with 1.0–2.5 mm particle size.

Keywords: residue; thermal; reactor; model; factorial

Biomass thermal processes have attracted much attention in recent time. Pollution problems arising from fossil fuels and residue accumulations, climate change mitigation, and protection of the environment and security of energy, among others are contending issues surrounding human activities (Boateng et al. 2006; Aquino et al. 2007; Putun et al. 2007). Driven by the need to widen the production of fuels and chemicals and substitutes biomaterials for those being manufactured from petrol chemicals, biomass conversion technology is extensively researched (Williams, Nugranad 2000; Zanzi et al. 2002; Sims 2003). In comparison to fossil fuel, biomass is environmentally friendly and renewable and can be processed into a variety of products, including fuels and chemicals (Yorgun, Simsek 2008; Demiral, Ayan 2011). In addition, it has higher volatile matter content and high ignition stability, thus it can be easily processed thermochemically into higher value fuels, such as methanol (C_2H_2OH) and hydrogen (H_2) (Zhang et al. 2010).

The range of biomass materials being investigated for energy resource has widened to include crop residues, herbaceous and woody crops and dedicated energy crops (Boateng et al. 2006). The use of bioresidues as a source of energy is a viable option to partially meet the world energy needs and solve environmental problem associated with waste disposal (Glassner et al. 1999; DiPardo 2000; Wilhelm et al. 2004). The energy within biomass can be released directly as heat or transformed into solid, liquid and

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gaseous fuels either by the biochemical/biological or thermochemical processes. In comparison to the biochemical/biological processes, the thermochemical processes via combustion, gasification, liquefaction or pyrolysis have higher efficiencies in terms of the lower time required and the superior ability to destroy most of the organic compounds (Miranda et al. 2009; Zhang et al. 2010). Biomass pyrolysis process can yield biochar, pyrolytic oils and gaseous products comprising H_2, CO, CO_2 and lower molecular weight hydrocarbon gases. A gas mixture rich in CO and H_2 (syngas) can itself be converted to mixed alcohols in processes similar to Fischer Tropsch process. Also the process generally results in enhanced heating value of the biochar product as compared to the feedstock (Boateng et al. 2006; Cantrell et al. 2008).

Sandbox, *Hura crepitans* tree is traditionally grown as an ornamental and shade tree in most parts of the world and is relatively in abundance in Nigeria. Each individual tree can produce up to 100 fruits or more yearly (Francis 1990). The fruit capsules containing mainly shells have little or no value in Nigeria. This unutilised shell residue materials constituting environmental sanitation problem from residue accumulation can therefore be upgraded to a renewable energy material to solve the sanitation problem and provide a clean alternative fuel. In this study, results are presented for sandbox shell as feedstock for biochar production in a laboratory batch pyrolysis process as affected by the heating temperature, heating time and particle size of feedstock from the pyrolysis process.

MATERIAL AND METHODS

Material. The biomass material used is sandbox shell. The sandbox tree is a member of the spurge family, Euphorbiaceae. It is mostly grown as an ornamental and shade tree in most part of the world due to its attractive dark green foliage (Francis 1990). The fruits produced are pumpkin shaped seed pods which are usually green when fresh and brown when dry. They mature in about three months after flowering and are about 6–9 cm in diameter depending on the size and with individual trees producing up to 100 fruits or more. The fruit is characterised by its tendency to break with an explosive sound when ripe and dry, splitting the seedpods into segments along the distinct radial line and catapulting the seeds as far as 100 m. Depending on the size of the fruits, the shell content is measured to vary from 85–92% wt. of the fruit, while the seed content varies from about 7–12% wt. Apart from the former use of its unexploded ripe fruits as dispensers of sand in the drying of ink on manuscripts, the whole fruit to make wheels for children's toys or the dolphin-shaped seed shells (mericarps) in necklaces, the inedible fruit still remain largely unutilised residue material, especially in Nigeria.

Material preparation and pyrolysis experiment. Shelled sandbox shells used for the study were collected from the University of Ibadan, Oyo State in South-western Nigeria. After the removal of extraneous materials, the shells sample were first processed into smaller sizes using a PC 400 × 300 hammer mill equipped with a 20 mm sieve and further ground in a Retsch SM 250 heavy duty grinding machine (Retsch GmbH & Co. KG, Haan, Germany) into fine particle sizes. The fine shell sample was then sieved to fractions with 0 –1.0, 1.0–2.5 and 2.5–5.0 mm particle sizes (diameter of particle size of sandbox shell feedstock).

The pyrolysis experiments were performed on 30 g of the particle sizes in a laboratory batch pyrolysis process consisting of a 250 ml round bottom flask reactor. The reactor is equipped with an adaptor, a reflux condenser unit and a condensate receiver. The reactor was heated externally by a thermostatically controlled furnace. The furnace was pre-heated to the desired temperature level before introducing the loaded reactor into the furnace to complete the set up. The experiments were carried out at 400, 500 and 600°C heating temperature and at 10, 20, and 30 min heating time. The gases and volatiles produced in the reactor pass through the reflux condenser unit into the condensate receiver. The non-condensable volatiles are vented out at the condensate receiver. The biochar product was determined by weighing the residual biochar left in the reactor after pyrolysis. The biochar yield was then defined as the percentage ratio of the weight of biochar remaining in the reactor after pyrolysis to the weight of the raw feedstock loaded into the reactor before pyrolysis.

Statistical analysis. The experiment was designed by applying response surface methodology through a three-factor full factorial design using Eesign Expert 6.8.0 software. The range and levels of the process parameters with the coded values

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Table 1. Experimental range and levels of process variable values used

Parameters	Variable values		
	–1	0	+1
A: heating temperature (°C)	400	500	600
B: heating time (min)	10	20	30
C: particle size (mm)*	0–1.0	1.0–2.5	2.5–5.0

*diameter of particle size of feedstock

used are as given in Table 1. The design matrix proposed by the software contained 32 experimental runs with six replicates at the centre points. The experiments were then carried out according to the design matrix and the experimental values of the output computed in the design matrix to determine the yield. The independent variables; heating temperature, heating time and particle sizes were correlated to the response variable; the biochar yield by the quadratic equation, Eq. (1).

$$Y = A_0 + \sum A_i X_j + \sum A_{ji} X_i^2 + \sum A_{ij} X_i X_j \qquad (1)$$

where:

Y – response

A_0, A_i, A_{ii}, A_{ij} – coefficients of the intercept, linear, square and interaction effects, respectively

X_i, X_j – coded independent variables

The regression model was statistically analysed using the software and analysis of variance used to evaluate adequacy of the developed model, the significance of the factors and their interactions, the related coefficients, the lack-of-fit and R-squared (R^2) tests. The parameters in the ANOVA having an *F*-statistics less than 0.05 probabilities are said to be significant factors. The coefficient of determination, R^2 statistic is a measure of the percentage of the variability of the parameter that is explained by the model, the higher the R^2 value the better the model (Abnisa et al. 2011; Dairo et al. 2011).

RESULTS AND DISCUSSION

Development of model equation

The quadratic polynomial model developed from the analysis in terms of the coded values is presented by Eq. (2):

$$Y = 36.6 - 1.51A - 1.32B - 1.23C + 0.15A^2 - 0.39B^2 - 1.77C^2 + 0.22AB + 0.71AC - 1.60BC \qquad (2)$$

where:

Y – biochar yield (% wt.)

A – heating temperature (°C)

B – heating time (min)

C – particle size (mm)

Results of analysis of variance (ANOVA)

The analysis of variance (ANOVA) indicating the significance of the factors and their interactions, the related coefficients, the lack-of-fit and R^2 tests are presented in Table 2. The probability of the model *P*-value of 0.0001, with an *F*-value of 16.32 at 95% confidence level implied that the model suggested by the software was significant. The obtained coefficient of determination, R^2 value of 0.8698 and a non-significant lack-of-fit as determined by the ANOVA ($P < 0.05$), indicated a good fit of the data to the model. This implied that the response quadratic model, Eq. (2), obtained adequately represented the actual relationships of the experimental factors within the ranges of experimental study considered. Besides the model, *A*, *B*, *C*, C^2, *AC* and *BC* terms, with $P < 0.05$ (Table 2) are significant terms in the model affecting biochar yield. The predicted R^2 of 0.6479 which indicates how well the model predicted the response is in reasonable agreement with the goodness-of-fit measure,

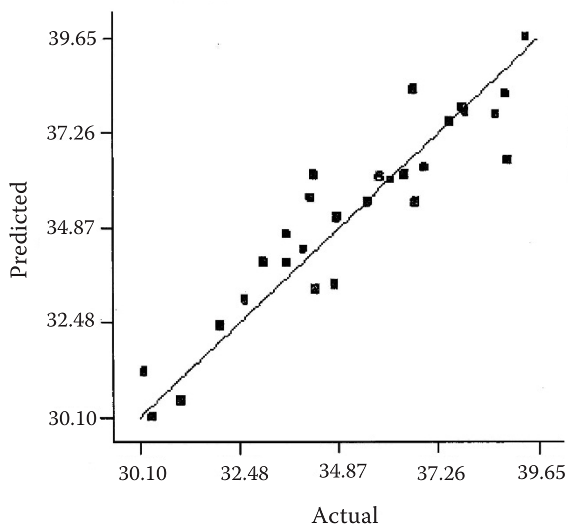

Fig. 1. Plot of the predicted versus actual values of char yield

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Table 2. ANOVA for response surface quadratic model

Source	Sum of squares	DF	Mean square	*F*-value	Prob > *F*	Remarks
Model	159.99	9	17.78	16.32	< 0.0001	significant
A	41.10	1	41.10	37.74	< 0.0001	significant
B	31.50	1	31.50	28.92	< 0.0001	significant
C	27.11	1	27.11	24.89	< 0.0001	significant
A^2	0.15	1	0.15	0.14	0.7121	
B^2	1.09	1	1.09	1.00	0.3273	
C^2	22.47	1	22.47	20.64	0.0002	significant
AB	0.59	1	0.59	0.55	0.4680	
AC	6.12	1	6.12	5.62	0.0269	significant
BC	30.82	1	30.82	28.30	< 0.0001	significant
Residual	23.96	22	1.09			
Lack of fit	23.96	17	1.41			
Pure error	0.000	5	0.000			
Cor. total	183.95	31				
R^2 = 0.8698; Adj-R^2 = 0.8165; Pred-R^2 = 0.6479; Adeq Precision = 16.380						

F – factor; R^2 – coefficient of correlation; Adj-R^2 – adjusted coefficient of correlation; Pred-R^2 – predicted coefficient of correlation; Adeq Precision – adequate precision; Cor. total – correlation total; DF – degrees of freedom

the adjusted R^2 of 0.8165. The comparison between the predicted and actual values of the biochar yield as shown in Fig. 1 implied that a good correlation between the process parameters and the response could be drawn by the model developed.

Effect of operating variables

The effect of the operating parameters was evaluated by response surface methodology using contour and three dimensional graphs. The ANOVA

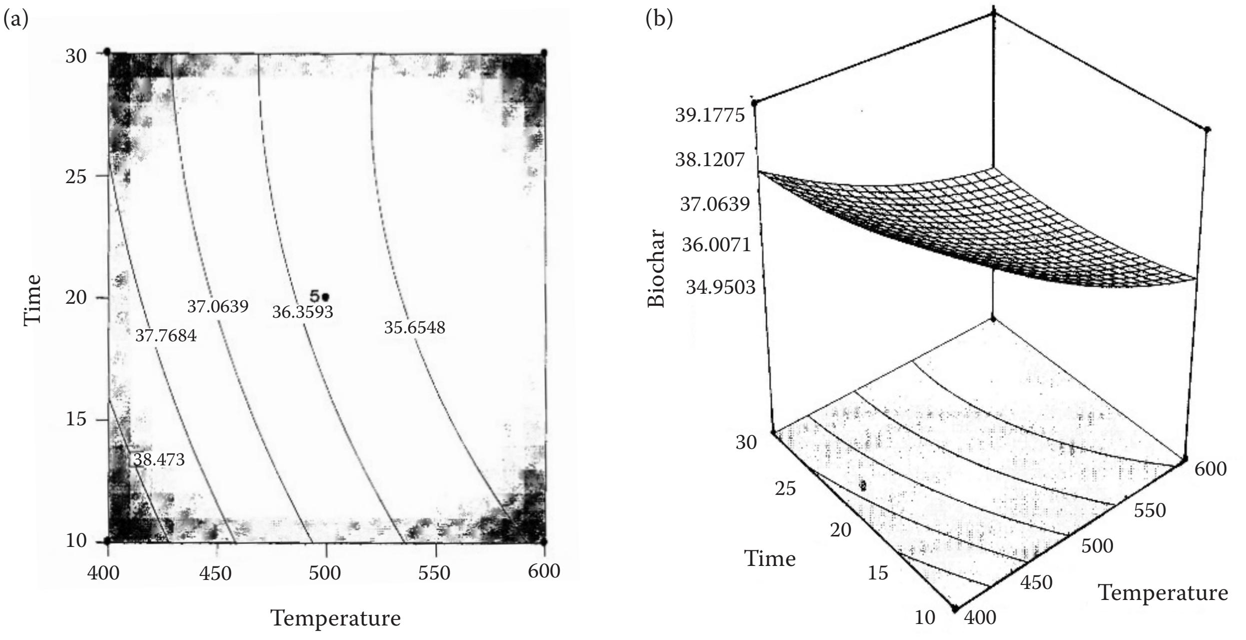

Fig. 2. Response surface plot as influenced by (a) heating temperature and (b) heating time at constant particle size

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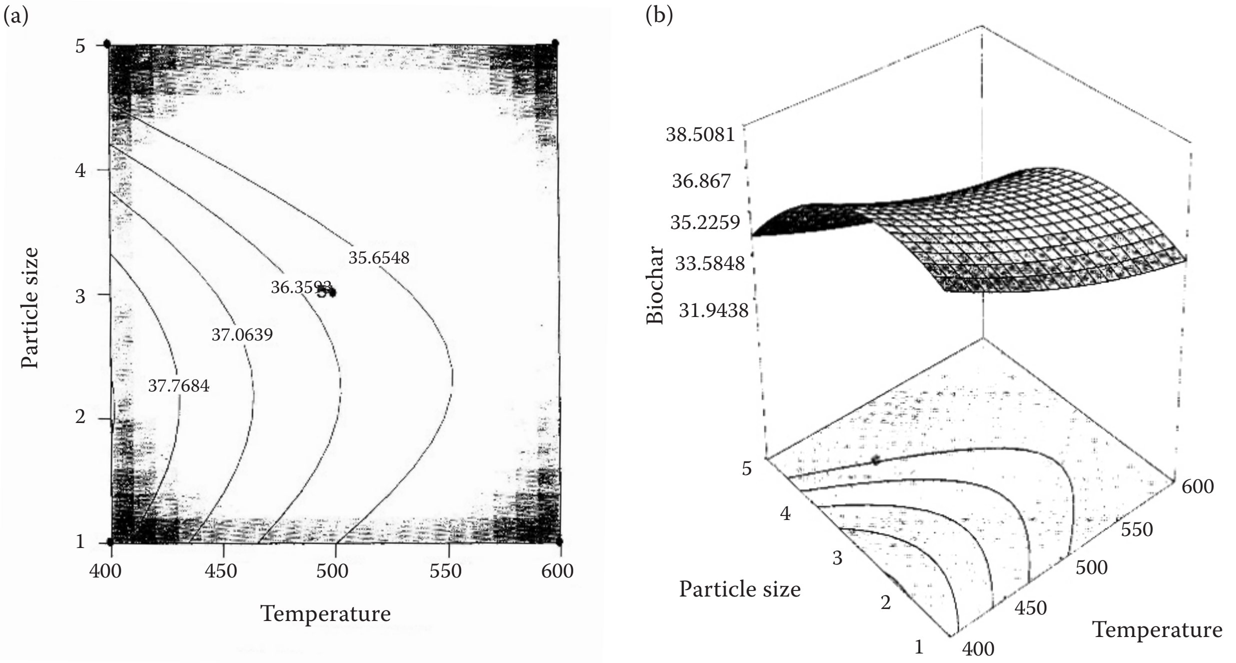

Fig. 3. Response surface plot as influenced by (a) heating temperature and (b) particle size at constant heating time

showed that the three parameters had significant effects on biochar yield. As a single factor, the heating temperature which had the highest F-value of 37.74 was the most influential factor as shown in the ANOVA Table 2. The combined effect of heating temperature and heating time is shown in Fig. 2 in form of contour and three dimensional surface graphs. In these graphs the particle size is held constant at the centre point of 1.0–2.5 mm. It is observed from Fig. 2a that surface area decreased with increases in heating temperature and heating time. Fig. 2b however shows that biochar yield decreased with increase in heating temperature. This effect that biochar yield decreased with increasing

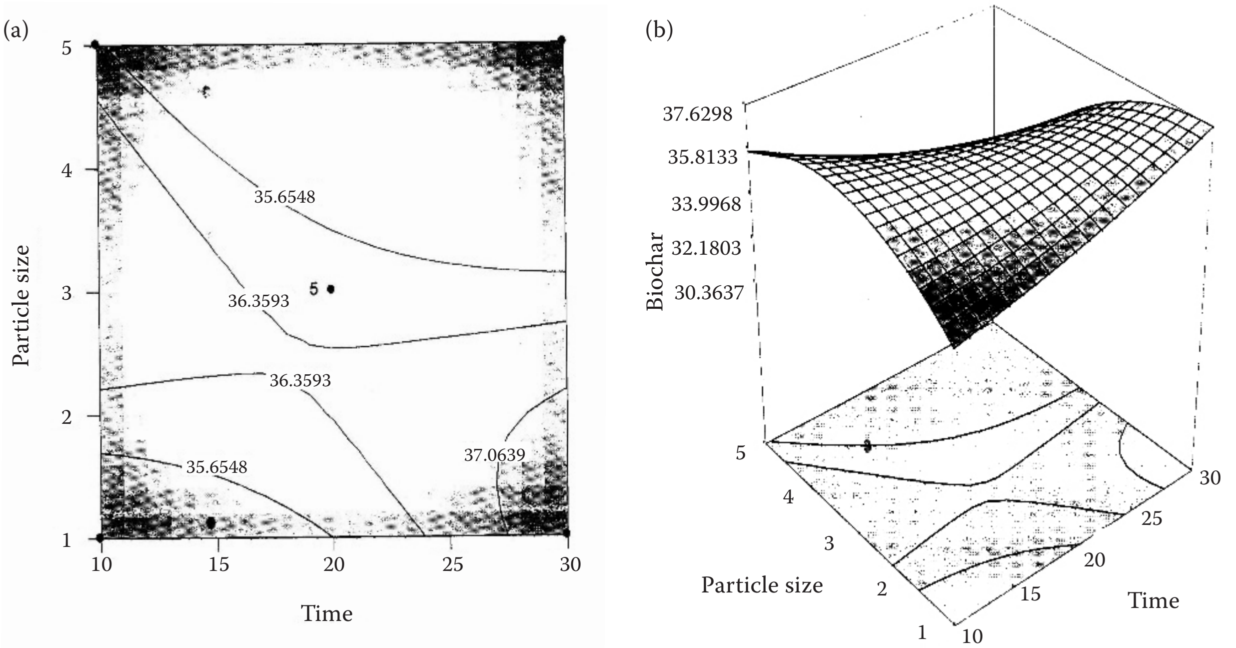

Fig. 4. Response surface plot as influenced by (a) heating time and (b) particle size at constant heating temperature

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heating temperature was also reported by other researchers (Boateng et al. 2006; Aquino et al. 2007; Putun et al. 2007). Decrease of biochar with increase in heating temperature is attributed either to greater primary decomposition of biomass at higher heating temperature or through secondary decomposition of the biochar residue (Williams, Nugranad 2000; Zanzi et al. 2002; Demiral, Ayan 2011). Max. biochar yield of 39.65% wt. occurred at 400°C heating temperature and 10 min heating time with 1.0–2.5 mm particle size.

The response surface graph of the interaction between the heating temperature and particle size with the heating time held constant at the centre point of 20 min is shown in Fig. 3. It can be observed from the contour of Fig. 3a that biochar yield increased with increase in particle size and decrease in heating temperature. On the other hand it is depicted from Fig. 3b that with increase in particle size, increase in biochar yield occurred but the biochar yield decreased as the particle size was increased further. A similar result was reported by Senzor and Kaynar (2006), where an increase in particle size results in greater temperature gradient inside the particle. So that at a given time the core temperature is observed to be lower than the surface, therefore giving rise to an increase in solid yields with a corresponding decrease in liquids and gases. In addition, particle size controls the rate of drying and primary pyrolysis and the extent of overlap of these processes (Neves et al. 2011). Max. biochar yield as 38.24% wt. was obtained at 400°C heating temperature and 0–1.0 mm particle size with 20 min heating time (Ertas, Alma 2010).

The combined effect of heating time and particle size with the heating temperature held constant at the centre point of 500°C is depicted in Fig. 4, respectively. It is observed from Fig. 4a that surface area decreased with increase in heating time and particle size. Fig. 4b showed that biochar yield decreased with increase in heating time. Maximum yield of 37.79% wt. was obtained at 10 min heating time and 1.0–2.5 mm particle with 500°C heating temperature.

CONCLUSION

The pyrolysis of sandbox shell in a laboratory batch pyrolysis process was conducted varying the heating temperature, heating time and particle size of feedstock. A three-factor full factorial experimental design of the response surface methodology was applied for the analysis of results. The adequacy of the quadratic polynomial model obtained was evaluated by analysis of variance. The results showed that the model gave good estimation of biochar yield with an F-value of 16.32 at 95% confidence level and coefficient of determination, R^2 value of 0.8698. The three parameters evaluated had significant effects on the biochar yield. However, the heating temperature was the most effective followed by the heating time and particle size of feedstock. Max. biochar yield of 39.65% wt. occurred at a heating temperature of 400°C and 10 min heating time with 1.0–2.5 mm particle size.

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