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PYROLYSIS OF MANGO STONE SHELL: EFFECT OF HEATING TEMPERATURE AND RESIDENCE TIME ON PRODUCT YIELDS

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ABSTRCT

Biomass residues, from which energy can be harnessed through thermo-chemical processes to mitigate climate change and enhance energy security, abound through agricultural activities. Mango (*Mangifera indica*) stone residues, if not harnessed, constitute a waste disposal problem in the environment during peak production period. Pyrolysis potentials of mango (Saigon Variety) stone shell was therefore investigated with the aim of characterizing the raw mango stone shell and identify production conditions for maximizing pyrolysis product yields. The process parameters that have been investigated were heating temperature and retention time. The experiment was conducted using a fixed bed reactor consisting of a 250 ml round bottom flask equipped with an adaptor, reflux condenser unit and condensate receiver with a thermostatically controlled furnace. The raw mango stone shell feedstock was prepared, dried and ground to particle sizes with $0 < d_p < 1.0$ mm. The experiment was designed by applying response surface methodology through a two-factor hexagonal factorial design using design expert 6.8.0 software. In view of this the batch process was carried out at five levels of heating temperatures of 300, 350, 400, 450 and 500 ^{o}C for three levels of residence times of 10, 20 and 30 min. The two variables significantly affected product yields, with temperature being the most effective. The quadratic polynomial models obtained explains adequately the modeled responses with R^2 values of 0.9992, 0.9872, and 0.8919 for the biochar, biooil and biogas yields, respectively. Maximum yields with the accompanying optimal conditions were found to be 55.60 wt% at 300 ^{o}C and 20 min, 36.73 wt% at 500 ^{o}C and 20 min and 24.0 wt% at 400 ^{o}C, 20 min for the biochar, biooil and biogas, respectively. The heating value and carbon, hydrogen, nitrogen, ash, moisture content, volatile matter and fixed carbon contents of the raw mango stone shell were found to be 21.74 MJ/kg, 44.63, 4.2, 0.35, 1.89, 1.86, 65.28, 18.4 wt%, respectively. The main composition values were 34.68, 16.63 and 20.17 wt% for cellulose, hemicellulose and lignin contents respectively.

Key words: Mango, Pyrolysis, Reactor, Design, Shell

1.   INTRODUCTION

Biomass residues, from which energy can be harnessed through thermo-chemical processes to mitigate climate change and enhance energy security, abound through agricultural activities. Mango stone residues, if not harnessed, constitute a waste disposal problem in the environment during peak production period.

The common mango or Indian mango, *Mangifera indica* is one of the most important fruit crop in the *Anacardiaceae* (Cashew or poison ivy) family with world-wide popularity. It is

indigenous to the Indian subcontinent and Southeast Asia (Fowomola, 2010). The fruit is extensively exploited for food, juice, flavor, fragrance and color and a common ingredient in new functional foods often called superfruits. Annual production worldwide is estimated at about 38.66×10^9 Kg. Nigeria is ranked 10th with a production estimate of 7.90×10^9 kg among the world's producers (FAOSAT, 2010). Mango fruit have a shorter shelf life when stored in ambient conditions and are sensitive to chiling injury when stored below 10^oC (Al-Hag and Sugiyama, 2004). The major wastes of mango processing are peels and stones (seeds), representing from 35 – 60% of the total fruit weight depending on the variety (Schieber et al., 2001). Because these byproducts represent a serious disposal problem and potential severe pollution problems, ways of sustainable production are been searched. This would solve the problem of waste treatment and increase the revenue made from the whole fruit (Mahila et al., 2001; Al-Hag and Sugiyama, 2004).

The utilization of mango wastes as a source of fat, natural antioxodants, starch, flour, feed and nutraceutical products respectively, has extensively been investigated in developed countries (Berardini et al., 2005). Peel has been found to be a good source of phytochemicals such as polyphenols, carotenoids, vitamin E, dietary fibre and vitamin C and also exhibited antioxidant properties. The seed kernel has potent antioxidant activity with relatively high phenolic contents (Ashoush and Gadallah, 2011). The export of mango pulp as a raw material for the production of some of these products was estimated at 62% of the total exports of fruits and vegetables in India, the world's largest mango producer (Berardini et al., 2005). Studies on the utilization of these wastes, particularly the seed shell in developing countries such as Nigeria are scarce. From the large quantities of mango fruits produed yearly, only little quantities are processed and exported (Yusuf and Salau, 2007). The peel and stone generated is not currently utilized for any commercial purpose; it is discarded as waste as it is of little or no food or industrial value in Nigeria (Falade et al., 2004). However the seed kernel has been found to be a good source of energy or carbohydrate in monogastric animal diets (Odunsi and Farinu, 1997). Based on the production statistics, from $2.56 \times 10^8 – 4.38 \times 10^8$ Kg of the wastes are generated annually in Nigeria. Hence, pyrolysis potentials of mango stone shell was investigated with the aim of characterizing the raw mango stone shell and identify production conditions for maximizing pyrolysis product yields from the mango stone residues.

2.0   EXPERIMENTAL

2.1   Sample Material and Preparations

Ripe mango fruits, the Saigon (cherry) (Falade et al., 2004) variety chosen for the study were harvested from identified mango trees from a private Farm in Ogbomoso, Oyo State, South West Nigeria. Harvesting was done during the fruiting season, from march – May, 2012. Piror to use, the fresh fruits were pulped and the seeds sun dried and cut into halves to separate seed kernels from shells. The empty shells were further sun dried, sawn into pieces and ground into fine particles using Retsch SM 250 heavy duty grinding mill. The ground particles were classified by the method prescribed by AOAC (2005) using Octagon-digital-4748-02, Tyler Standard Sieves set and the shaker to obtain fine particle sizes with $0 < d_p < 1.0$ mm, where d_p is the diameter of particle size of feedstock. Oven drying at $105\ ^oC$ for 24 hrs to a constant weight (borne dried) in a Uniscope SM 9053, Laboratory Oven as prescribed by AOAC (2005) was conducted (Bridgwater et al., 1999). The basic physico-chemical properties such as the ultimate, proximate and main composition properties were analyzed following ASTM Standards; D 5373 for carbon, hydrogen and nitrogen, D 4239 for sulphur, D 3177 for ash and weight fraction of oxygen were determined by difference. Moisture content was determined by weight loss at $105\ ^oC$ for 48 hrs (AOAC, 2005). The heating value was estimated from the

elemental values with the correlation proposed by Channiwala (2002). The results of the analysis are presented in Table 2.1.

The mango stone shell sample had 44.63 % carbon and 34.45 % oxygen contents. The values recorded for the nitrogen (0.53 %) and sulphur contents (0.41) are lower than that found in some shells (Miranda *et al.,* 2009). Implying fewer emissions or corrosion during utilization of the shell for power production (Vamvuka and Sfakiotakis, 2011). The shell had 65.28 % volatile content, which is considered high and desirable for a good regulation of combution and gasification processes. The heating value of 21.74 MJ/Kg obtained for the mango stone shell indicated its potential as a feedstock material for pyrolysis process.

Table 2.1: Physico-chemical Properties of Mango Stone Shell

Ultimate Analysis		Proximate Analysis		Ligninocellulosic Analysis	
Carbon, %	44.63	Ash, %	1.89	Cellulose, %	34.68
Hydrogen, %	4.2	Moisture Content,%	1.68	Hemicellulose, %	16.63
Oxygen, %	34.45	Volatile matter, %	65.28	Lignin, %	20.71
Nitrogen, %	0.53	Fixed Carbon, %	18.4		
Sulphur, %	0.41	Density, g/cm^3	11.84		
Chlorine, %	0.3	Heating value, MJ/Kg	21.74		

2.2. Pyrolysis Process and Analysis

The apparatus for the batch pyrolysis process was made up of a glass reactor, which was heated by a temperature-controlled furnace. The reactor was connected externally to a pair of reflux condenser, with water circulation and a condensate receiver placed in an ice block jacket. The pyrolysis system was equipped with glass adaptors which serve as interface between the reactor inside the furnace and condenser outside. The experiment was designed by applying response surface methodology through a two factor hexagonal factorial design, requiring 10 experiments was employed using design expert 6.8.0 software. In view of this, the batch process was carried out at five levels of heating temperatures of 300, 350, 400, 450 and 500 ^{o}C for three levels of residence times of 10, 20 and 30 min. For each run, 50g of sample was weighted into the reactor. The timing was based on an initial experimental run at 300 ^{o}C, wherein volatilization was observed to cease within 8 - 10 min. of the start of the operation, thus the minimum time was set at 10 min. The pyrolysis products included biochar, biooil and biogas products. The biochar residue was retained inside the reactor in the furnace chamber. The biooil product was comprised of the tar condensed on the wall along the pyrolysis line and condensed hydrocarbon collected at the condensate receiver. Both products were determined gravimetrically and percent yields were obtained based on the initial weight of mango fed, while the biogas yield was determined from material balance.

3. RESULTS AND DICUSSION

3.1 Statistical Analysis Models

The results obtained for the actual yield, predicted yield and the residual values of three response variables, biochar, biooil and biogas yields are presented in Table 3.1. The predicted values of the responses were evaluated from second order model fitting techniques utilizing Design Expert 6.0.8 Software. The quadratic model suggested by the software for the biochar,

Table 3.1: Experimental Order, Actual Yield, Predicted Yield and Residual

SDO	Biochar Yield			Biooil Yield			Biogas Yield		
	AY	PY	RD	AY	PY	RD	AY	PY	RD
1	15.85	15.82	0.033	6.88	6.98	-0.10	5.61	6.57	-0.96
2	14.60	14.63	-0.033	8.50	8.40	0.100	6.90	6.89	-0.0065
3	12.77	12.74	0.033	10.54	10.64	-0.10	6.69	7.10	-0.41
4	12.87	12.90	-0.033	10.75	10.65	0.100	6.38	6.92	-0.54
5	13.40	13.37	0.033	10.46	10.56	-0.10	6.14	6.55	-0.41
6	14.35	14.38	-0.033	9.23	9.13	0.100	6.42	6.41	-0.0065
7	12.88	12.89	-0.010	9.60	9.79	-0.19	7.52	6.74	0.78
8	12.87	12.89	-0.020	9.99	9.79	0.20	7.14	6.74	0.40
9	12.92	12.89	0.030	9.88	9.79	0.087	7.20	6.74	0.46
10	12.89	12.89	0.000	9.70	9.79	-0.093	7.41	6.74	0.67

SDO= Standard order, AY= Actual yield, PY= Predicted yield, RD= Residual

biooil and biogas response variables and the corresponding model equations in terms of the coded values were as presented in Equations 3.1, 3.2 and 3.3, respectively.

$$Y_c = 12.89 - 1.46A - 0.11B + 1.47A^2 + 0.70B^2 - 0.51AB \qquad 3.1$$

$$Y_o = 9.79 + 1.83A - 0.19B - 0.98A^2 + 0.18B^2 + 0.47AB \qquad 3.2$$

$$Y_g = 7.32 + 0.17A + 0.30B - 1.32A^2 - 0.60B^2 + 0.04AB \qquad 3.3$$

Where $Y_c = $ Biochar yield, wt% , $Y_o = $ Biooil yield, wt% , $Y_g = $ Biogas yield, wt% , A = Heating temperature, ^{o}C and B = Residence time, min. The significance of the statistical model of these equations were evaluated by F-test analysis of variance (ANOVA) (Table 3.2). The value of prob > F less than 0.05 in Table 3.2 revealed that the quadratic model of the response variable was significant at 95% confidence level. The probability of model F-statistic value was 0.0001, 0.0007 and 0.0457 for the biochar, biooil and biogas yields, respectively as shown in Table 3.2. These implies that the models suggested for the biochar, biooil and biogas response variables by the software were significant models. Besides the models, A, B, A^2, B^2 and AB model terms had significant effect on the biochar yield. Similarly, A and A^2 model terms were found to be significant for the biooil yield and A^2 term for the biogas yield.

The statistical parameters obtained from the ANOVA for the developed models are presented in Table 3.3. These parameters were used to established the accuracy of the developed models. The biochar yield model showed a relatively high determination coefficient, R^2 value of 0.9992 and low coefficient of variation, C.V of 0.33. The corresponding values are 0.9872 and 2.04, and 0.8919 and 4.49 for the biooil and biogas yield models, respectively. The closer the determination coefficient to unity, the better the model suits the experimental data, indicating less difference between the calculated and measured values.

The models adequacy were also evaluated by adjusted R^2, Predicted R^2 and predicted error sum of squares (PRESS). A good model is indicated by large R^2 and low PRESS (Myers and Montgomery, 2002). In this case R^2 = 0.8919, Adj R^2 = 0.7568, Pred R^2 = -1.9148, Adeq Precision = 6.449 and PRESS = 9.69 for biogas yield. A negative predicted R^2 implies that the overall mean was a better predictor of the response than the current model suggested for the biogas yield. Adeq precision measures the signal to noise ratio and a ratio greater than 4 is desirable. Table 3.3 showed ratios of 88.544, 24.283 and 6.44 for the biochar, biooil and biogas

Table 3.2: Analysis of Variance (ANOVA) and Lack of Fit

Source	Sum of Squares	DF	Mean Square	F- Value	Prob > F
Char Yield Model	9.86	5	1.97	977.90	<0.0001
A	6.37	1	6.37	3156.51	<0.0001
B	0.036	1	0.036	17.90	0.0134
A^2	2.88	1	2.88	1428.69	<0.0001
B^2	0.65	1	0.65	320.89	<0.0001
AB	0.19	1	0.19	96.00	0.0006
Residual	8.067E-003	4	2.017E-003		
Lack of fit	6.667E-003	1	6.667E-003	14.29	0.0325
Pure Error	1.400E-3	3	4.667E-004		
Cor Total	9.87	9			
Liquid Yield Model	11.76	5	2.35	61.77	<0.0007
A	10.10	1	10.10S	265.35	<0.0001
B	0.11	1	0.11	2.77	0.01711
A^2	1.27	1	1.27	33.47	<0.0044
B^2	0.043	1	0.043	1.12	<0.3488
AB	0.16	1	0.16	4.31	0.1065
Residual	0.15	4	0.038		
Lack of fit	0.060	1	0.060	1.95	0.2569
Pure Error	0.092	3	0.031		
Cor Total	11.91	9			
Gas yield Model	2.97	5	0.59	6.60	<0.0457
A	0.092	1	0.092	1.02	<0.3692
B	0.27	1	0.27	2.95	0.01609
A^2	2.33	1	2.33	25.95	<0.0070
B^2	0.48	1	0.48	5.33	<0.0822
AB	1.225E-003	1	1.225E-003	0.014	0.9127
Residual	0.36	4	0.90		
Lack of fit	0.26	1	0.26	8.37	0.0629
Pure Error	0.095	3	0.32		
Cor Total	3.33	9			

Table 3.3: Statistical parameters obtained from the ANOVA for the model equations

Variable	Biochar	Biooil	Biogas
Standard Deviation, SD	0.045	0.20	0.30
Mean	13.54	9.55	6.74
Coefficient Variation, CV	0.33	2.04	4.49
R Squared, R^2	0.9992	0.9872	0.8919
Adjusted R^2	0.9982	0.9712	0.7568
Predicted R^2	0.9754	0.8049	-1.9148
Adequate Precision	88.544	24.283	6.449
PRESS	0.24	2.32	9.69

yield models respectively. Indicating an adequate signal, and that each of the models can be used to navigate the design space.

## 3.2   Effect of Pyrolysis Parameters on Product Yields

The three dimentional response surfaces and contour plots of the mango stone shell pyrolysis product yields are depicted in Figure 3. These figures showed the combined effect of heating temperature (A) and residence time (B) on the product yields of biochar (a), biooil (b) and biogas (c) products, respectively. The biochar yield at constant residence time decreased as the heating temperature is increased from 300 to 500 ^{o}C as shown in Figure 3.1a. Maximum biochar conversion for the mango stone shell was obtained as 16.68 wt% at a heating temperature of 300 ^{o}C and residence time of 20 min. In case of the biooil yield as the response variable (figure 3b), increasing the heating temperature and the residence time, decreases the bioil yield. The maximum biooil yield conversion of 11.03 wt% was obtained at a heating temperature and residence time of 500 ^{o}C and 20 min, respectively. On the other hand, the combined effect of heating temperature and residence time had a parabolic effect on biogas yield, Figure 3c. Biogas yield increased with increases in both heating temperature and residence time up to a value and decrease with further increases in both parameters. The maximum biogas yield conversion was obtained as 7.36 wt% at 400 ^{o}C heating temperature and 20 min residence time. The decreasing trend of the solid product with respect to temperature was consistent with biomass pyrolysis reports of Boateng *et al.,* 2006 and Zanzi *et al.,* 2002. The decrease in biochar yield was attributed to either greater primary decomposition of the feedstock or through secondary decomposition of the solid product (Ertas and Alma, 2010). While the decrease in biooil and biogas yields at lower temperature was attributed to incomplete decomposition. And the decrease in biooil and biochar yields and increase in biogas yield at higher temperature is corroborated to be due to secondary cracking of vapor and solid products (White *et al.,* 2011).

4.0   CONCLUSIONS

The optimum process conditions for pyrolysis product yields from mango stone shell were determined using a two factor hexagonal factorial design in response surface methodology. It was observed from ANOVA that the two factors had significant effects on the response variables. Quadratic models developed for the yield of biochar, biooil and biogas had R^2 values of 0.99, 0.98 and 0.89, respectively. Maximum yield with the accompanying optimal conditions of biochar, biooil and biogas obtained were 16.68 wt% (at 300 ^{o}C and 20 min), 11.03 wt% (at 500 ^{o}C and 20 min) and 7.36 wt% (at 400 ^{o}C and 20 min), respectively. The raw mango stone shell had heating value, nitrogen, ash, and fixed carbon contents of 21.74 MJ/kg, 0.35, 1.89, 18.4 wt%, respectively. The shell residue is a potential feedstock material for pyrolysis process.
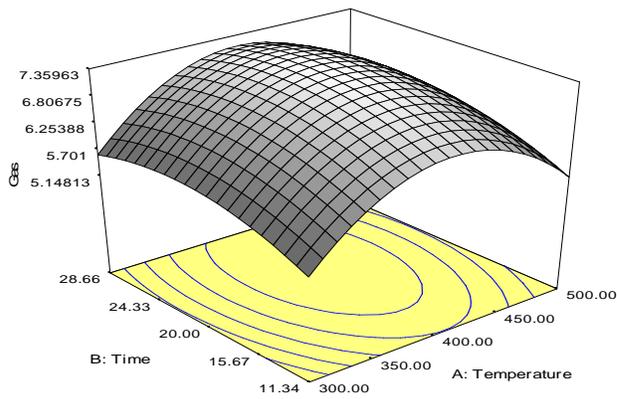
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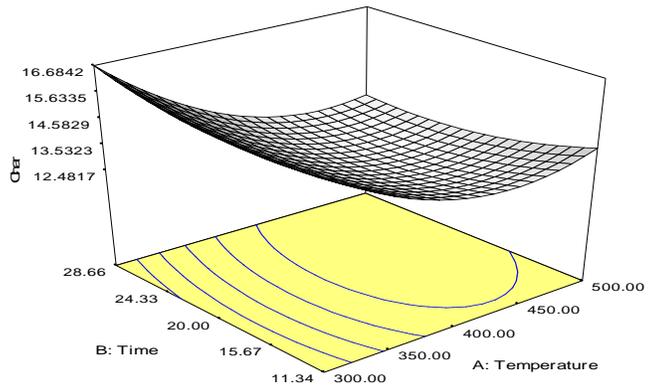
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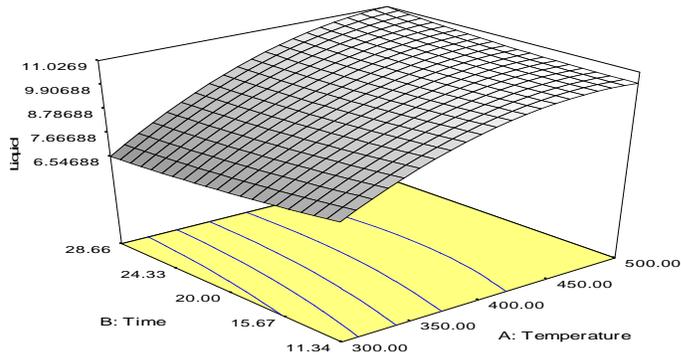
b

c

Figure 3.1: The Response Surfaces and Contours of Mango Stone Shell Pyrolysis Product
Yields; a) Biochar Yield, b) Biooil Yield and c) Biogad Yield

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