EXPERIMENTAL OPTIMIZATION OF BIO-OIL YIELD FROM COCONUT SHELL PYROLYSIS USING BOX BEHNKEN DESIGN.

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ABSTRACT
Pyrolysis of coconut shell for maximum yield of bio- oil in a fixed bed reactor was investigated in this study. Box Behnken design of experiment in the Response Surface Methodology (RSM) was used to investigate the effect of temperature (400, 500 and 600^{o}C), reaction time (5, 10 and 25 minutes) and feed particle size (6, 9.5 and 13 mm) on the yield of bio-oil. RSM was used to estimate the optimum conditions for maximum yield of bio-oil. Preliminary pyrolysis experiment showed that bio-oil increased with temperature up to 500^{o}C where it was thermally decomposed into gas and then reduced to minimum. Other pyrolytic products (char and gas) were also significantly influenced by temperature, time and feed particle size. The coefficient of determination (R^2) of the model of bio-oil yield in terms of temperature, time and size was 0.9893 at $p < 0.05$. The maximum bio-oil yield was 47.00% at 486.67 ^{o}C, 22.78 minutes and 6.78 mm and these was experimentally verified. The pyrolysis oil obtained at these optimum process conditions was analysed using Fourier Transform Infrared Spectroscopy (FTIR) and the oil yield obtained agreed with the predicted value with percentage absolute error of 0.85%.

Keywords: Coconut, pyrolysis, bio-fuel, optimization, kinetics

Introduction

Fossil fuel production and utilization are being bedeviled by several challenges like the depletion rate due its nonrenewable nature, the growing demands resulting in high oil prices and the environmental pollution associated with its combustion products (Sundaram and Natarajan, 2009). Quest to overcome these problems make renewable energy sources like biomass attractive.

Biomass are biological hydrocarbon materials, most often referring to plants or plant-derived materials consisting of carbon, hydrogen, oxygen, nitrogen and some other components in small proportion (Tsamba *et al.,* 2006). Biomass include wide range of materials such as: virgin wood from forestry, energy crops specially grown for energy applications, agricultural residues from agriculture harvesting, food waste from food and drink preparation and processing, and post-consumer waste, or industrial waste and co-products from manufacturing and industrial processes.

Biomass provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security (Monique *et al*, 2003). Its energy can be obtained through biochemical or thermochemical conversion. Biochemical conversion makes use of the enzymes of bacteria and other micro-organisms to break down biomass while thermo-chemical conversion processes use heat or chemicals to convert biomass into other products. Some of the basic techniques are: gasification, combustion, pyrolysis, and gasification (Dermirbas, 2007).

Pyrolysis is a thermal decomposition technique which decomposes carbonaceous bio wastes into liquids, gases, and char (solid residue) in the absence of oxygen at elevated temperatures. Pyrolysis consists of a very complex set of reactions involving the formation of radicals. The products are divided into volatile fractions consisting of gases, vapours and tar components and a carbon – rich residue (Demirbas, 2009). Pyrolysis product yields and their distributions over the whole range of temperature depend not only on feedstock composition and operating temperature, but also on the specific characteristics of the system used, such as size and type of reactor, efficiency of heat transfer from the hot reactor surface to and within the biomass, feed particle size, and vapor residence time (Joardder *et al*., 2011)

Agricultural waste is one of the members of biomass, which is an attractive renewable energy resource because it is widely dispersed and could contribute zero net carbon dioxide emission to the atmosphere (Joardder *et al*, 2011). Abundance and availability of agricultural by – products make them good sources of raw materials for many processes. Harvesting and processing of crops results in the generation of considerable wastes which are usually inexpensive to get. Many researches have been carried out on such by – products as, rice husk, tobacco seed, sugarcane, and even coconut shell in the production of activated carbon for adsorption purposes (Wei *et al*, 2008).

Coconut shell is a waste of plant origin that is a renewable source of energy in the form of biomass. It has been used extensively as adsorbent for various metals and dye in the activated form (Amuda *et al*., 2007; Sartape *et al*., 2012; Mohd Iqbaldin *et al*., 2013; Rolence *et al* ,2014). Studies have also been carried out to assess its availability as a resource for energy in the face of inadequate power supply to meet the need of man (Azam *et al*, 2009). In Nigeria, extensive agricultural practices are done and the by - products can be employed as biomass for energy generation (Tsai, 2006). Conversion of coconut shell into pyrolytic oil by fixed bed fire – tube heating reactor has been studied by varying the reactor bed temperature, running time, gas flow rate and feed particle size. The maximum liquid yield of 34.3 wt % was obtained at 450 °C for a feed size of 0.6mm, gas flow rate of 6 litre/minute. The pyrolysis oil obtained at these optimum conditions were analyzed for physical and chemical properties to be used as an alternative fuel (Joardder *et al*, 2011). Bio- oils have been produced from coconut shell with or without catalysts via fast pyrolysis and one such catalyst employed has been zeolite. The pyrolysis has been carried out in a fixed bed reactor with maximum yield of 38.93 wt % at temperature of 491.57 °C, particle size of coconut shell of 12.5 mm and nitrogen flow rate of 5 ml/min (Kongmum and Ratanawilai, 2014).

Considering the maximum yield of bio-oil obtained from the previous studies, its potentials as an additive for fuel on commercial scale might not be feasible. Hence, the present study is focused on the analysis of the combination of process variables to improve the yield of the bio-oil derivable from the pyrolysis of coconut shell using statistical optimization approach.

Materials and Methods

Cocnut shell preparation and characterization

Coconut Shells (CS) were collected from a local market in Ogbomoso. The CS were washed with water to remove the debris and then sun dried for 24 h. It was crushed and then oven dried at a temperature of 105°C to a constant weight. The dried CS was further crushed and screened to three particle sizes (< 6mm, 6 - 9.5mm and > 9.5mm). Proximate and ultimate analysis were carried out on the dried CS using ASTM methods.

Pyrolysis procedure

The pyrolysis experiments were conducted in a stainless steel fixed-bed reactor (ID: 38.4 mm, length 280 mm). The reactor was heated externally by an electric furnace with the temperature being measure by a thermocouple fixed in the reactor and controlled by an external PID controller. The process variables were in the range of 400 – 600°C for temperature, 5 - 25 minutes for time and 6-13mm for particle size. After pyrolysis, the bio-oil was condensed and collected in the reagent bottles. The bio-oil at the optimum condition was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The uncondensed gases were flared to the atmosphere while the char was removed from the reactor. Coconut shell of 200g weight was used for each run of the experiment. The percentage yields of the bio- oil and char were calculated using equation 1 while the bio-gas was calculated as the balance.

$$Yield(\%) = \frac{Desired \quad Product(g)}{Coconut \quad shell(g)} x100 \qquad (1)$$

Experimental design and data analysis

Design Expert software version 6.0.8 (STAT-EASE Inc., Minneapolis, USA) was used to design the experiments using Box-Behnken Design (BBD) with three factors and three levels in the Response Surface Methodology (RSM).The dependent variable selected for this study was the bio- oil yield, expressed in percentage (%), and the independent variables chosen were the temperature (A), reaction time (B) and particle size(C). Regression analysis of the experimental data to fit the response equation in terms of the factors was carried out and the quality of fit of the model was expressed by the correlation coefficient (R-squared) and Analysis of Variance (ANOVA). A second order polynomial equation was proposed to fit the experimental data as given in equation (2):

$$Y = a_0 + a_1A + a_2B + a_3C + a_{11}A^2 + a_{22}B^2 + a_{33}C^2 + a_{12}AB + a_{13}AC + a_{23}BC \qquad (2)$$

where Y is the predicted response for bio- oil yeild, a_0 is the value of the fitted response at the centre point of the design, a_i, a_{ii}, a_{ij} being the linear, quadratic, and cross product terms, respectively. A statistical optimization of the model was conducted using the RSM. The BBD was used to determine the main and interaction effects of all the process parameters. The ranges of all the factors studied are as given in Table 1. The actual values of the process variables and their ranges were selected based on the preliminary experiments. The optimum values of all the variables were obtained by solving the regression equations and by analyzing the contour and 3D surface plots.

Table 1: Range of levels for parameters used in the pyrolysis of coconut shell

Parameters	Range of levels		
	-1	**0**	**+1**
A: Temperature (°C)	400	500	600
B: Time (minutes)	5	15	25
C:Particle size (mm)	6	9.5	13

Results and Discussion

Characteristics of the coconut shell

The results of the proximate and ultimate analysis of the coconut shell are as presented on Table 2. The volatile content value is high (66.90%) compared with the fixed carbon contents (23.20 %) and ash content (1.40%). A higher volatile content of feedstock with lower amounts of fixed carbon and ash is desirable for higher percentage of liquid yields in the pyrolysis process. Higher amount of fixed carbon and ash content of a feedstock contribute to char formation. Moreover, water in liquid yield originates from the original moisture in the feedstocks and dehydration reactions occurring during pyrolysis (Prabhakar *et al.*, 1986; Czernik and Bridgwater, 2004; Joardder *et al.*, 2011). Feedstock used in the presented study was of a high volatile and low moisture, fixed carbon and ash contents.

Table 2: Proximate and ultimate analysis of coconut shell

Properties	Percentage
Proximate Analysis	
Moisture Content	8.50
Volatiles	66.90
Fixed carbon	23.20
Ash	1.40
Ultimate Analysis	
Carbon	54.20
Hydrogen	5.60
Nitrogen	0.62
Sulphur	0.08
Oxygen*	39.50

* Calculated by difference

Effect of temperature on the pyrolysis products yield

The percentage yields of bio-oil, char and gas in the pyrolysis of coconut shell at a temperature range between 400 - 600°C, particle size of 13mm and reaction time of 25 minutes are as presented on Figure 1. The yield of bio-oil increased gradually with the increasing temperature from 400°C to the maximum value at a temperature of 500°C and then decreased to a minimum value at 600°C. The gas yield increased over the whole temperature range, while char yield decreased over the whole temperature range. The low gas yield at lower temperature is due to incomplete decomposition of the coconut shell while the decrease in bio-oil and char yield at higher temperature are due to the secondary cracking of pyrolysis vapour and solid char resulting in production of more gas. The decrease in bio-oil yield and increase in gas yield above a temperature of 500°C may be due to decomposition of some oil vapors into permanent gases and secondary carbonization reactions of oil hydrocarbons into char. The result is similar to that of Islam *et al.*(2003), Asadullah *et al.*(2008), Joardder *et al.* (2011) and Chowdhury *et al.* (2014)

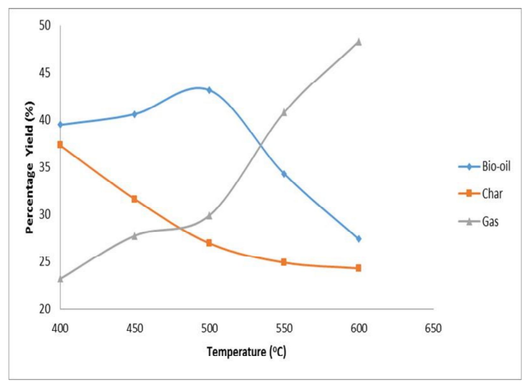

Figure 1: Effects of Temperature on the pyrolysis products' yield at 25 minutes and 13 mm particle diameter

Effect of time on the pyrolysis products yield

The effect of time on the coconut pyrolysis products yield at a temperature of 600°C and particle size of 13mm is as presented on Figure 2. The bio-oil yield increased gradually to the maximum at a time of 15 minutes and later on decreased to the minimum in 25 minutes. The gas yield was low at time less than 15minutes due to the incomplete pyrolysis but latter increased with time throughout the reaction period. The char yield decreased throughout the period of the pyrolysis due to the thermal decomposition of the coconut shell into the liquid and gaseous products. This phenomena is similar to that of the effect of temperature as earlier presented by Joardder *et al.* (2011) and Chowdhury *et al.* (2014).

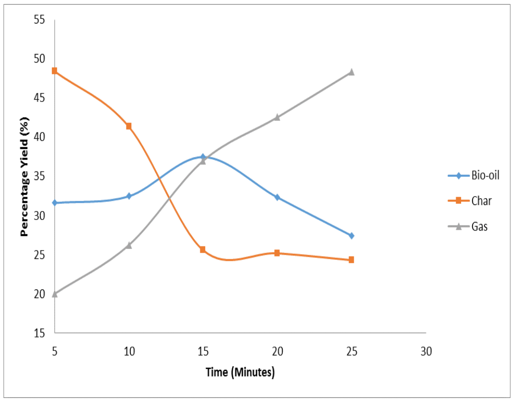

Figure 2: Effects of Time on the pyrolysis products' yield at 600°C and 13 mm particle diameter

Effect of particle size on the pyrolysis product yields

The variation in the pyrolysis products yield of coconut shell due to variation in the particle size of the feed at 600°C and 25 minutes reaction time is as presented on Figure 3. From the figure, the maximum bio-oil and char yields were at 6mm particle size and these reduced with increasing size. However, the gas yield increased with the increasing diameter of the feed particle. Smaller feed particle sizes provide more reaction surface and allow a high heating rate that leads to fast decomposition of the biomass. This phenomenon provides sufficient time for secondary reactions in the oil vapors and consequently gas yields increase while liquid and char yields decrease

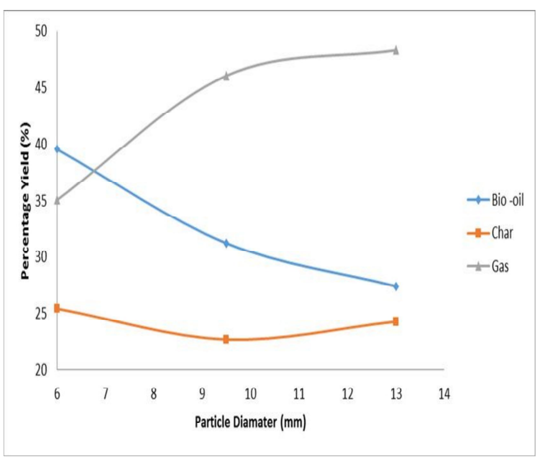

Figure 3: Effects of particle size on the pyrolysis products' yield at 600°C and 25 minutes

Box Behnken Design (BBD) for Pyrolysis of Coconut shell

The matrix of the BBD experimental design for the pyrolysis of coconut shell at various combinations of various temperature (A), time (B) and feed particle size (C) as well as the resulting products yield is as presented on Table 3. At each pair of experimental runs, run number 1 and 2; 5 and 6; 9 and 12 had the same process conditions with different time, results shows that bio-oil yield increased with increased time. This observation is due to the fact that as time increases, char gain enough time for thermal decomposition into liquid vapour (Joardder *et al*., 2011). Effect of different temperature were investigated at the same process condition of time and particle size as shown on runs 1 and 5; 7 and 11. As temperature decreased from 600°C to 400°C, the bio-oil yields decreased. This observation is consistent with previous result presented on Figure 1 which is in agreement with Chowdhury *et al*. (2014). The effect of changing feed particle size can be observed from the pairs of runs 7 and 13; 10 and 11 which is consistent with the result on Figure 3.

Table 3 Box Behnken Design (BBD) for bio-oil yield from pyrolysis of coconut shell

Run	Factors			Response
	Temperature (°C)	Time (Minutes)	Particle Size (mm)	Bio –oil yield (%)
1	600	25	9.5	31.24
2	600	5	9.5	9.5
3	500	15	9.5	39.48
4	500	5	6	9.56
5	400	25	9.5	37.83
6	400	5	9.5	4.86
7	600	15	13	37.46
8	500	25	6	43.01
9	500	5	13	4.61
10	400	15	6	36.41
11	400	15	13	29
12	500	25	13	43.13
13	600	15	6	39.8

Second Order Polynomial Regression Model and Statistical Analysis

The regression coefficients, standard error of coefficients, and p-values for the significant factors in the estimation of the bio-oil yield in terms of temperature (A), time (B) and feed particle size (C) are listed in Table 4. As a replica of equation (2) by substituting the coefficient with the corresponding value on Table 4 for the significant terms at $p<0.05$, equation (3) was obtained.

$$Y = 3.59 + 0.10A + 0.87B - 0.13C - 0.81B^2 - 0.22AB + 0.18BC \quad (3)$$

Equation (3) was used to evaluate the influence of process variables on the bio-oil yield (%). Analysis of variance method was employed to further estimate the significance and accuracy of the model. The corresponding results are presented in Table 5 where the model showed very high F value (92.06) and a very low probability value (p -value model = 0.001) for the system investigated. The

Predicted R-Squared value of 0.9379 is correspondently in reasonable agreement with the Adjusted R-Squared value of 0.9785. Adequate Precision measures the signal to noise ratio. A ratio > 4 is desirable. The ratio of 24.308 in this study indicates an adequate signal. This model can be used to navigate the design space. The coefficient of variation (CV) as the ratio of the standard error of estimate to the mean value of the observed response is a measure of reproducibility of the model, generally a model can be considered reasonably reproducible if its CV is not greater than 10 per cent. Hence, the low variation coefficient value (CV = 4.05%) obtained indicates a high precision and reliability of the experiments.

Table 4: Coefficients of Models of Bio –oil yield

Factors	Coefficient of Estimate	DF	Standard Error	p-Value
a_0	3.59	1	0.056	0.0001*
a_1	0.10	1	0.044	0.0589**
a_2	0.87	1	0.044	0.0001*
a_3	-0.13	1	0.044	0.0286*
a_{22}	-0.81	1	0.071	0.0001*
a_{12}	-0.22	1	0.063	0.0138*
a_{23}	0.18	1	0.063	0.0265*

***significant at p<0.05; **significant at p < 0.01**

Table 5: ANOVA for Response Equation of Bio –oil yield

Source	Sum of Square	DF	Mean Square	F- Value	p-value
Model	8.65	6	1.44	92.06	0.0001*
Residual	0.094	6	0.016		
Total	8.75	12			

*** Significant at $p < 0.05$; $R^2 = 0.9893$; Adjusted $R^2 = 0.9785$; Predicted $R^2 = 0.9379$**

Adequate Precision = 24.308, CV= 4.05 %

Pyrolysis Process Optimization

In order to acquire a maximum response value of the bio-oil yield from the pyrolysis of coconut shell, a numerical optimization function based on the BBD on Design Expert 9.0 version was employed to locate the values of independent variables. The optimality plots for the response variable are given in Figure 4. The profiles illustrate the composite desirability of the systems and the bio-oil yield (%) as a function of the factors. A desirability index of 1.000 with a maximum response value (47.00%) is obtained at A = 486.67^{o}C; B = 22.78 minutes; C = 6.78 mm. These optimum condition was verified experimentally and the bio-oil yield was 47.40%. The absolute error between the actual and predicted bio-oil yield is 0.85%. This maximum bio-oil obtained is higher than that of the previous studies 34.3% (Joardder *et al*, 2011) and 38.93% (Kongmum and Ratanawilai, 2014).

In order to further understand the effect of independent variables, 3D response surface plots based on the predictive quadratic model (Equation 3) for the bio-oil yield are plotted as shown on Figures 5-7. Effects of temperature and time at C = 6.78mm is as shown on Figure 3. The effects of temperature and particle size and that of time and particle size at the optimum values are as show on Figures 6 and 7, respectively.

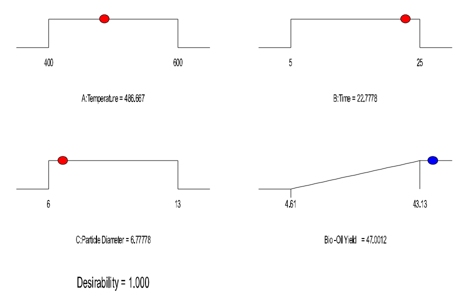

Figure 4: Ramps showing the optimized process concitions for bio-oil yield.

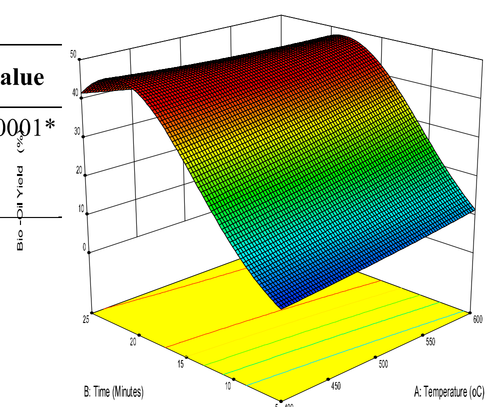

Figure 5: Effects of temperature and time on the coconut shell pyrolysis bio-oil yield (at C = 6.78 mm)

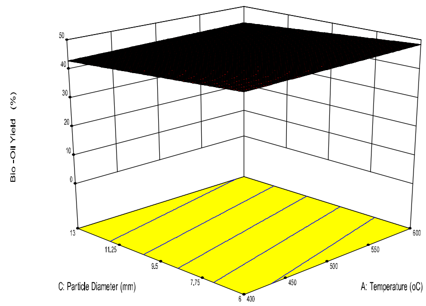

Figure 6: Effects of temperature and particle size on the coconut shell pyrolysis bio-oil yield (at B = 22.78 minutes)

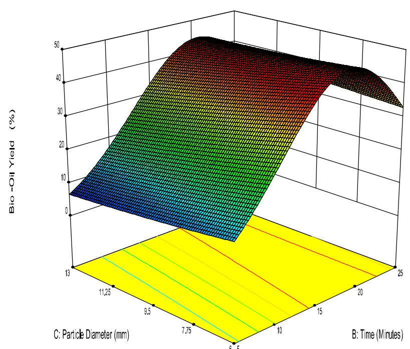

Figure 7: Effects of time and particle size on the coconut shell pyrolysis bio-oil yield (at A = 486.67 °C)

Chemical Characterization of the bio-oil at optimum condition.

The FTIR spectra of bio-oil obtained at the optimum condition is as shown on Figure 8 while the different assignments of the FTIR spectra of the bio-oil is a presented on Table 6. The bio-oil is mostly made up of alkane and alkenes**.**

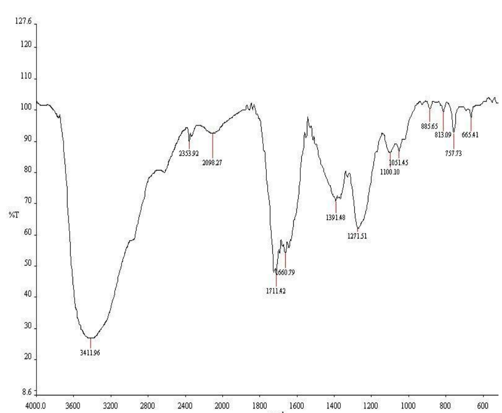

Figure 8: FTIR spectra of bio-oil

Table 5: Peaks and functional groups from FITR of bio-oil.

Wave number (cm -1)	Type of vibration	Functional group
3411.96	H–bonded O–H stretch (Broad strong band)	Alcohol/Phenol
2353.92	Doublet	Carbon dioxide
2098.27	C≡C stretch (medium)	Terminal alkyne
1711.42	C=O stretch (strong)	Ketone or Carboxylic acid
1660.79	C=C stretch (medium)	Alkene
1391.48	C=C stretch (medium)	Aromatic
1271.51	C–O stretch	Alcohol
1100.10	C–O stretch	Ether
1051.45	C–O stretch	Ether
885.65	C–H bend	Aromatic
813.09	C–H bend	Aromatic
757.73	C–H bend	Aromatic
665.41	C–H bend	Aromatic

Conclusions

This study demonstrated efficacy of BBD experimental design in estimating the influence of interaction of pyrolysis variables on the bio-oil yield from coconut shell pyrolysis. The bio-oil yield was influenced positively by temperature and time while particle size had negative influence linearly. The increment in the interactive factor of temperature and time reduced the bio-oil yield while that of time and particle size increased the yield. The reduced second-order polynomial quadratic regression model for the responses of bio-oil yield was significant. Finally, the maximum yield of bio-oil predicted by the model was in agreement with the experimental value while the oil produced possessed the required chemical properties.

References

Amuda, O.S.; Giwa, A.A. and Bello, I. A. (2007). Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochemical Engineering*, 36(2):174-181.

Asadullah, M. A.; Rahman, M. M.; Ali, M.A.; Motin, M.B.; Sultan, M. R.; Alam, M. and Sahedur R. M. (2008). Jute stick pyrolysis for bio-oil production in fluidized bed reactor. *Bioresource Technology,* 99:44–50.

Chowdhury, R.; Poddar, S. and De, S. (2014) Kinetic Modelling of Non – Catalytic Pyrolysis of Waste Jute in a Fixed Bed Pyrolyzer. *APCBEE Procedia* , 9:18 – 24.

Czernik, S. and Bridgwater, A. V., 2004. Overview of applications of biomass fast pyrolysis oil. *Energy and Fuels*, 18: 590-598.

Demirbas, A. (2007). Effects of temperature and size on bio-char yield from pyrolysis of agricultural residues. *Journal of Analytical and Applied Pyrolysis,* 72:243-248.

Demirbas, A. (2009). Biofuels from agricultural biomass. *Energy Sources Part A*, 31:1573–1582.

Islam, M.R.; Islam, M.N. and Islam, M.N., (2003).Fixed bed pyrolysis of sugarcane bagasse for alternative liquid fuel production. *Proceedings of International Conference on Mechanical Engineering, ICME2003, 26-28 December. BUET,* Paper No.: ICME03-TH-16.

Joardder, M. U. H.; Islam, M. R.; and Beg, M. R. A. (2011). Pyrolysis of coconut shell for bio – oil. *Proceedings of the International Conference on Mechanical Engineering, ICME011, Dhaka, Bangladesh*, 1 – 6.

Kongmum, P. and Ratanawilai, S. (2014). Catalytic pryrolysis of coconut shell for bio – oil. *International Journal of Advances in Chemical Engineering and Biological Sciences*, 1(1): 127-130.

Mohd Iqbaldin, M.N.; Khudzir, I.; Mohd Azlan, M.I.; Zaidi, A.G.; Surani, B. and Zubri, Z. (2013) Properties of coconut shell activated carbon. *Journal of Tropical Forest Science,* 25(4): 497–503.

Monique, H.; Andr'e, F.; Richard van den, B.; G-oran, B.; Dolf, G. and Wim, T. (2003). Exploration of the ranges of the global potential of biomass for energy. *Biomass and Bioenergy*, 25: 119 – 133.

Prabhakar, K.; Maheshwari, R. C. and Vimal, O. P. (1986). Pyrolysis of coconut shell and its potential for fuel. *Agricultural Wastes*, 17(4): 313 -317.

Rolence, C.; Machunda, R.L. and Njau, K.N. (2014). Water hardness removal by coconut shell activated carbon. *International Journal of Science, Technology and Society*, 2(5): 97-102.

Sartape, A.; Mandhare, A.; Salvi, P.; Pawar, D.; Raut,P.; Anuse, M. and Kolekar, S. (2012) Removal of Bi (III) with Adsorption Technique Using Coconut Shell Activated Carbon. *Chinese Journal of Chemical Engineering*, 20(4):1-9

Sundaram, E. G. and Natarajan E. (2009). Pyrolysis of coconut shell: an experimental investigation. *Journal of Engineering Research,* 6(2): 33-39.

Tsai, W.T. (2006). Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal of Analytical and Applied Pyrolysis*, 76: 230-237.

Tsamba, A. J.; Yang, W. and Blasiak, W. (2006). Pyrolysis characteristics and global kinetics of coconut and cashew nut shells. *Fuel Processing Technology*, 87: 523-530.

Wei, L.; Kunbin, Y.; Jinhui, P.; Libo, Z.; Shenghui, G.; and Xia, H. (2008). Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars. *Industrial Crops and Products*, 28: 190-198.