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Effect of Oxygen on Biochar Yield and Properties

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***Abstract*—**Air infiltration in mass scale industrial applications of bio char production is inevitable. The presence of oxygen during the carbonization process is detrimental to the production of biochar yield and properties. The experiment was carried out on several wood species in a fixed-bed pyrolyser under various fractions of oxygen ranging from 0% to 11% by varying nitrogen and oxygen composition in the pyrolysing gas mixtures at desired compositions. The bed temperature and holding time were also varied. Process optimization was carried out by Response Surface Methodology (RSM) by employing Central Composite Design (CCD) using Design Expert 6.0 Software. The effect of oxygen ratio and holding time on biochar yield within the range studied were statistically significant. From the analysis result, optimum condition of 15.2% biochar yield of mangrove wood was predicted at pyrolysis temperature of 403 ^{o}C, oxygen percentage of 2.3% and holding time of two hours. This prediction agreed well with the experiment finding of 15.1% biochar yield.

***Keywords*—**Mangrove wood, slow pyrolysis, oxygen infiltration.

I. Introduction

THE increase scarcity of fossil fuels makes the pursuit of alternative fuels increasingly important. Furthermore, fossil fuels are often implicated with the environmental degradation due to the release of greenhouse gases, rogue natural disasters blamed on climate change and acid rain [1]. The utilisation of biomass waste such as agricultural and forestry by-products are perceived with great commercial appetite thus becoming an important subject matter in many bio-energy fields. It holds promising future in countries with huge agricultural sector because the utilisation of this inexpensive and renewable resource not only provides a cleaner form of energy to fulfil the energy demand but also offers a solution to the waste disposal problem.

For decades, studies on biochar, a form of alternative fuel produced by pyrolysis of various plant precursors containing high carbon content had been carried out from for various applications. Pyrolysis comprises of three stages: moisture and volatile loss, followed by formation of primary biochar and finally the formation of secondary biochar. The final products are biochar, bio-oil and gases, where fraction of each is determined by the decomposition of key chemical components of the biomass; cellulose, hemicelluloses and lignin [2]. The optimum pyrolysis condition is critical for biochar yield and quality. It determines the suitability of biochar to fit the intended applications; soil conditioning [3-5], pollutant's absorbent [6], fuel pellet [7] and catalysts support [8] in which heating value, porosity, surface area and pore size are important quality criteria which are largely controlled by operating conditions such as pyrolysis temperature, particle size, heating rate and holding time.

Wood-derived biochar such as from mangrove plant is widely used as solid fuel. It also has excellent sorption capacity to store essential nutrients for plants thus had been applied in soil as carbon fixation method. It is appeared as a hard and heavy charcoal which is normally produced by kilning the mangrove wood logs over a lengthy eight to ten days at 220°C followed by baking process for another two weeks at 83 °C [9]. Nonetheless, traditional charcoal production technique contains several loopholes such as the lack of established fact regarding the optimum temperature for biochar yield, while studies on other biomass found that biochar is formed favourably at lower pyrolysis temperature, lower sweeping gas rate and longer holding time to allow secondary coking and repolymerisation reactions [1]. Moreover, studies conducted on the effect of oxygen infiltration are limited, although such phenomenon is very likely to occur in large scale production plant. A study on the effect of oxygen concentration on pyrolysis of olive waste solid found that increased oxygen concentration did not affect the decomposition of hemicellulose which marked the first volatilisation stage but caused the oxidation of char to occur at lower temperature i.e. 295°C compared to 335°C in the absence of oxygen [10]. Similar conclusion was also made regarding oxygen concentration effect on decomposition of cellulose.

The aim of this work is to study the influence of oxygen concentration on biochar yield by carrying out pyrolysis of fixed size wood samples under inert atmosphere (0% oxygen) and oxidative atmosphere (up to 11.0% oxygen) and to establish fact on optimum pyrolysis temperature and holding time condition for wood-based biochar.

II. Materials and Methods

A. Materials

Several wood species which are commonly used as raw materials in the charcoal and biochar production were used as the feedstock. In this report, mangrove wood obtained directly from a mangrove forest is used as the main feedstock. The samples were cut into about 1cm cubes and dried in an oven for about 24 hours at 60°C.

The gross calorific value of biomass is determined using a bomb calorimeter according to the ASTM D5865-11A (1999)

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test procedure [11]. The proximate analysis of mangrove wood are conducted according to the ASTM D3172-07A (1997) test procedures [12] and the ultimate analysis was conducted according to the ASTM D3176-09 (1997) test procedures [13].

The proximate and ultimate analyses of mangrove wood are shown in Table I.

TABLE I
PROXIMATE AND ULTIMATE ANALYSIS OF MANGROVE WOOD SOLID WASTE

Proximate Analysis		Ultimate analysis	
Contents	***wt%***	***Element***	***wt%***
Volatile	55.65	C	44.09
Fixed Carbon and Ash	21.61	H	5.06
Moisture	7.24	N	0.28
		O	50.00*
LHV	16.38 MJ/kg	S	0.57

**by weight difference*

B. Fixed Bed Pyrolysis Experiment

The experiment was conducted in a fixed bed pyrolyser system as shown in Fig. 1. The dimensions of the stainless steel main reactor are 52 mm diameter × 150 mm height. Several uniformly distributed holes were made through the sample bed to make sure the gas pass and distributed evenly through the samples. There is gas pre-heat area to ensure the required gas temperature can be attained in before entering the main reactor. Both pre-heat zone and main reactor are fixed with three sets of ceramic band of total 1.5 kW and individually controlled by PID controllers. At the top of the main reactor, a K-type thermocouple was used which has range of temperature between 0K to 1200K. There is also exhaust exit at the top of the main reactor to ensure the internal pressure will maintain at 1atm. The pyrolysis gas was not collected and discharged into the atmosphere.

Oxygen and Nitrogen gas were mixed prior to entering the reactor. The gas mixed ratio was determined by controlling gas flow valve of both oxygen and nitrogen at a certain flow rate. The reactor is designed so that samples can be place and taken out by pulling out top cover of the main reactor.

About 50g sample was used in each experiment. Nitrogen gas was used to sweep out the air in the reactor for about 10 minutes before starting the experiment. Experiment was carried out under gas flow containing oxygen between 0% and 11% at flow rate of 200ml/min. The heating rate is set to 10K/min. The experiments were conducted in difference temperature, oxygen ratio and residence time. The char obtained from the pyrolysis was collected and analyzed.

C. Response Surface Methodology

Response surface method (RSM) was employed as design of experiment (DOE) method. RSM investigated the effect of temperature, oxygen percentage and holding time on biochar yield.

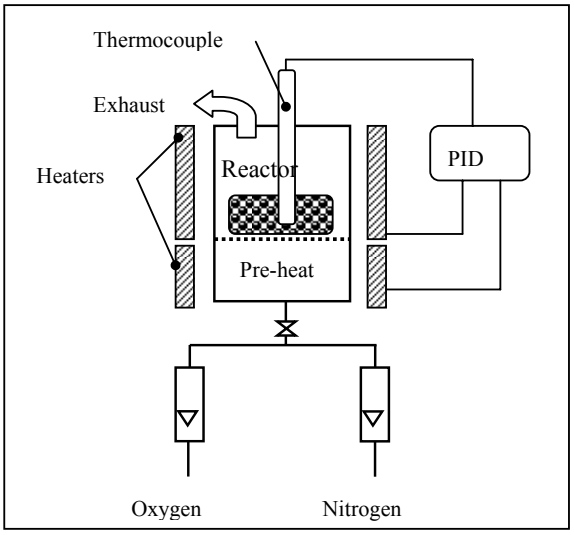

Fig. 1 Schematic Diagram of Fixed Bed Pyrolysis System

The advantage of RSM is fewer experimental trials required, by assigning parameter's values at certain points on geometric design shape such as cube plus extrapolated points known as alpha. This allows the observation on point to point effect of parameter within the range studied as well as predicting its effect within alpha which can be described by a model.

The first step of RSM is selecting the parameters and specifying the low and high values (lower and upper extreme) of each as shown in Table II. This design information was fitted into RSM's central composite design (CCD) to produce an experimental design shown in Table III.

TABLE II
PARAMETERS AND RANGE UNDER STUDY

Factor	Units	Low	High
Temperature	C	400	560
O_2 percentage	%	2.29	9
Holding time	hour	2	4.25

III. RESULT AND DISCUSSION

A. Gross Calorific Value

Gross calorific value of selected biochar yields are shown in Table IV. The yield from run 9, 11, 13 and 16 were selected from several experimental runs shown in Table III in order to compare each yield in terms of different temperature, oxygen ratio, and holding time.

The calorific value of the biochar is significantly higher than mangrove wood (16 MJ/kg). The temperature parameter of yield obtained from run 9 and run 16 are 345°C and 480°C respectively. The yield from run 16 has higher energy content than the yield from run 9 which are 25.64 MJ/kg and 24.64 MJ/kg respectively. Higher pyrolysing temperatures contribute to the higher energy content of the biochar.

TABLE III
DESIGN OF EXPERIMENT CCD

Run	A: Temperature (°C)	B: Oxygen percentage (%)	C: Holding time (hour)	Yield Percentage (%)
1	400	2.3	2.00	15.10
2	560	2.3	2.00	9.09
3	400	9.0	2.00	7.54
4	560	9.0	2.00	16.19
5	400	2.3	4.25	4.64
6	560	2.3	4.25	0.95
7	400	9.0	4.25	1.31
8	560	9.0	4.25	1.26
9	345	5.6	3.13	17.05
10	614	5.6	3.13	2.25
11	480	0	3.13	22.39
12	480	11.3	3.13	1.31
13	480	5.6	1.23	17.88
14	480	5.6	5.02	1.31
15	480	5.6	3.13	4.49
16	480	5.6	3.13	1.10
17	480	5.6	3.13	1.06
18	480	5.6	3.13	1.32
19	480	5.6	3.13	1.44
20	480	5.6	3.13	1.68

TABLE IV
GROSS CALORIFIC VALUE

Run	Energy (MJ/kg)
9	24.64
11	31.56
13	30.69
16	25.64

Run 16 has higher oxygen ratio than run 11 which are 5.6% and 0% respectively as shown in Table III. The yield from run 11 has higher energy content than the yield from run 16 which are 31.56 MJ/kg and 25.64 MJ/kg respectively. In the presence of oxygen, the energy content will decrease due to oxidation of the char.

Run 16 has longer holding time than run 13 which are 3.13 hours and 1.23 hours respectively. The yield from run 16 has lower energy content than the yield from run 13 which are 25.64 MJ/kg and 30.69 MJ/kg. The longer holding time, energy content of the yield will increase in the presence of oxygen.

B. Thermal Decomposition of Mangrove Wood

Fig. 2 shows the weight changes at temperature 25-800 °C. Thermogravimetric (TG) profile provides thermal characteristics of biomass as a result of thermal degradation of its key elements such as hemicelluloses, cellulose and lignin. TG profiles of mangrove wood was typical to those of other biomass.

Initial weight loss (6.8%) observed at up 120 °C was attributed to moisture loss. Afterwards, another significant weight loss by almost 54.5% due to decomposition of biomass was occurred up to 470 °C. This leaves 21.6% residue as the remainder which consists of fixed carbon and ash. The decomposition of mangrove wood occurred in two stages; the first stage between 210-420 °C was ascribed to the decomposition of cellulose and almost a complete release of volatiles, whereas the residue after second stage above 420 °C is considered as char.

DTG curve exhibits fast decomposition at 340 °C, signalling high reactivity of cellulose responsible for its decomposition. Lignin also started to decompose above this point, but mass decrease is not noticeable due to its stable benzene rings. The smaller DTG peak at 280 °C indicates the decomposition of hemicellulose.

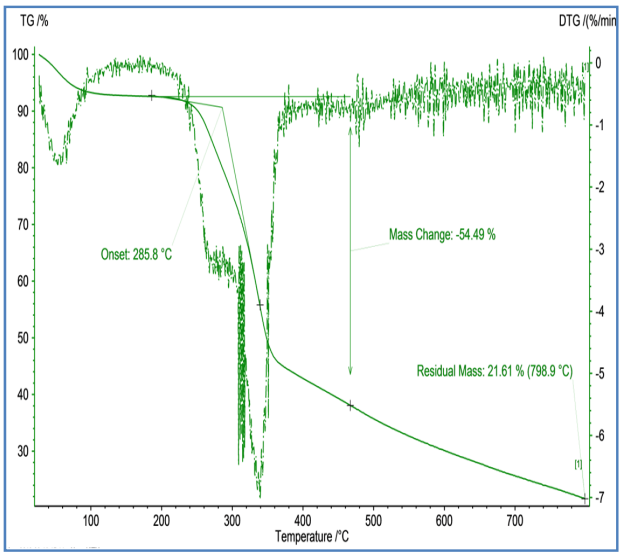

Fig. 2 Weight changes during pyrolysis of raw mangrove wood

C. Factor Affecting Biochar Yield

Process optimization was carried out by Response Surface Methodology (RSM) by employing Central Composite Design (CCD) using Design Expert 6.0 Software. Upon transformation suggested by Box-Cox plot, linear model of base log 10 was the best model to describe the variation of biochar yield attributed to the factors under investigation since it had insignificant lack of fit and F-value of 1.49. ANOVA test shown in Table V revealed that main factors B and C which represent oxygen percentage and holding time respectively were statistically significant with p-value < 0.05. The data are normally distributed as shown in the normal plot of residuals in Fig. 3.

TABLE V
ANOVA TESTS

Source	Sum of squares	DF	Mean square	F Value	Prob > F
Model	2.67	2	1.33	12.58	0.0004
B	0.53	1	0.53	4.97	0.0395
C	2.14	1	2.14	20.19	0.0003
Residual	1.80	17	0.11		
Lack of Fit	1.45	12	0.12	1.69	0.2923
Pure Error	0.36	5	0.07		
Cor Total	4.47	19			

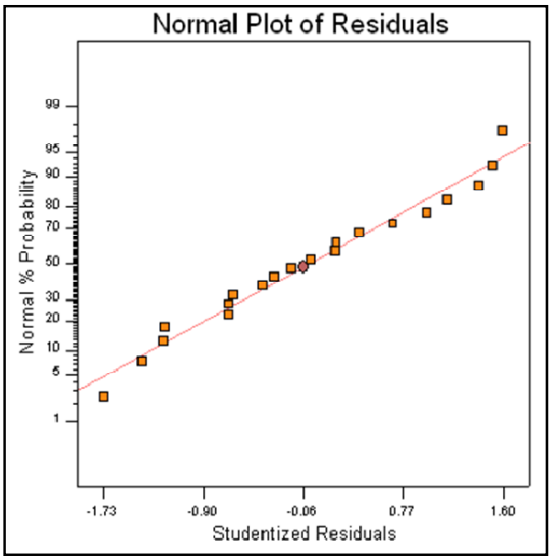

Fig. 3 Normal plot of residuals

RSM analysis found that maximum biochar can be achieved at lower pyrolysis temperature, shorter holding time and lower oxygen percentage as shown in Fig. 4. With regard to lower pyrolysis temperature, earlier study which reported high char yield at 400 °C whereas above 600 °C gas generation such as CO and CH_4 would be favoured [14]. Others reported steady decrease of char yield when temperature was raised from 300 °C to 700 °C [1, 15]. Such trend was due to release of most condensable volatiles as a result of hemicelluloses and cellulose degradation between 260 °C and 360 °C, as observed in aforementioned TG curve. There is possibility that most lignin, combustible gases and condensable liquid tar degraded at 420 °C, leaving the char as the only remain. Above this point, cellulose deviates further from degradation process which otherwise converts it into a more stable anhydrocellulose which favours char formation because its high molecular weight hydrocarbons starts to depolymerise into volatiles [16, 17].

Intuitively, decomposition of hemicelluloses and cellulose increased porosity of the char which encourages diffusion of oxygen. This allowed better reaction between polymers and oxygen which led to volatilisation, even the relatively more stable and less reactive lignin was not spared. The extent of polymers oxidation was reportedly increased with increasing oxygen concentration, as indicated by the decrease of decomposition temperature. Similar result was found on char oxidation in which CO release began at lower temperature in oxygen-rich environment and vice versa [10]. Such findings perfectly agreed with this study's observation regarding the unfavourable effect of increasing oxygen concentration on char yield.

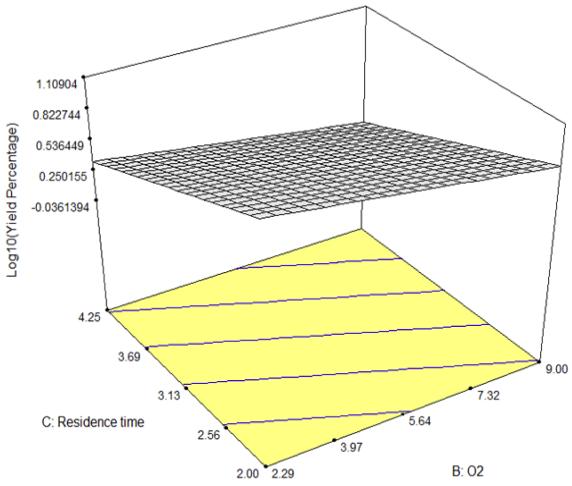

Fig. 4 Effect of operating parameters on char yield

The decrease of char yield was observed with longer holding time despite previous studies reported the increase of char yield with longer holding time [18]. This is due to the absence of oxygen during the pyrolysis in the latter. In oxidative atmosphere, the longer holding time possibly allows greater chance of oxygen to oxidize more biomass, though this is not proven statistically in the study. Hence, further study must be conducted to investigate about the relationship between oxygen presence and holding time.

IV. CONCLUSION

The effect of oxygen ratio and holding time on biochar yield within the range studied were statistically significant i.e. (α<0.05). Based on the model linear suggested by RSM during result analysis, optimum condition of 15.2% biochar yield was predicted at pyrolysis temperature of 403°C, oxygen percentage of 2.3% and holding time of two hours. This prediction agreed well with the experiment which obtained 15.1% biochar yield, thus validated the method. The study show that oxygen is the unfavourable effect presence in real application i.e. biochar yield decrease with increase oxygen composition. Biochar yield was 10.0% and 3.8% at 2.3% and 9.0% oxygen composition respectively.

Higher temperature will increase energy content of biochar yield. In the presence of oxygen, longer holding time will decrease energy content. This is due to oxidation of the biochar. Longer residence time will decrease energy content of biochar

in the presence of oxygen. However, further study on the relationship between oxygen presence and holding time must be conducted in the future to explain the decrease of char yield at longer holding time in the presence of oxygen.

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