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Optimization of Biochar Production from Slow Pyrolysis of Oil Palm Waste

Nur A. N. M. N. Azman[a], Mohd Asmadi[a,*], Muhammad A. S. Nawawi[a], Nor A. S. Amin[a], Zaki Y. Zakaria[a], Muzzakkir M. Zainol[b], Zul I. Z. Lubes[c], Natthanon Phaiboonsilpa[d]

[a]Chemical Reaction Engineering Group (CREG), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor Darul Takzim, Malaysia
[b]School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[c]Institute of Biological Sciences, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
[d]King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Rd. Ladkrabang, 10520 Bangkok Thailand
mohdasmadi@utm.my

The Malaysian palm oil industry has grown rapidly in recent years. An abundance of oil palm biomass is generated from the palm oil mil, including fronds, trunks, mesocarp fibre, shells, and empty fruit bunches (EFB). These oil palm wastes (OPW) were potentially converted into value-added products such as syngas, bio-oil, and biochar through thermochemical conversion technology. In this study, the optimization of OPW-derived biochar was conducted using the Box-Behnken design (BBD) and response surface methodology (RSM). The effects of pyrolysis temperature (400-700 °C), pyrolysis time (30-120 min), and nitrogen flow rate (0.4-1.0 L/min) on biochar yield were analysed. The results demonstrated the highest biochar yield (27.2 wt%) was obtained from pyrolysis of EFB at 550 °C for 75 min under 0.7 L/min N_2 flow. Then, other OPW sample namely oil palm trunk (OPT), oil palm frond (OPF), and palm kernel shell (PKS) were pyrolyzed at the optimum operating condition. The produced biochar was characterized with thermogravimetric analysis (TGA) and scanning electron microscope (SEM). The results show the highest yield and thermal stability of biochar produced from pyrolysis of PKS compared to other OPW samples. The surface features of PKS-derived biochar also displayed well-developed pores and a honeycomb-like shape. Hence, PKS can be optimized to obtain high-quality biochar.

1. Introduction

Oil palm waste (OPW) is the primary biomass generated in Malaysia. Approximately, 110 Mt of OPW are produced annually from the oil palm industry (Mohamed and Yusup, 2021). Massive production of OPW mainly comprises mesocarp fibres, oil palm frond (OPF), empty fruit bunch (EFB), and palm kernel shells (PKS). These abundant OPW have created a significant disposal problem. In palm oil mills, most OPW materials are generally disposed of through incinerators as fuel for electricity generation. The process releases flue gases that contain NO_x, CO and ash into the atmosphere that may cause air pollution. Thus, the current waste management must be improved accordingly based on thermochemical conversion technology to recover and recycle OPW into value-added products such as bio-oil, syngas, and biochar.
Pyrolysis technology is one of the thermochemical processes that have great potential for OPW conversion. The processing method occurs in oxygen-deficient conditions at moderate temperatures (400-600 °C) (Gautam et al., 2019). There are three types of pyrolysis processes namely slow, fast, and flash pyrolysis mode. All methods have a different heating rate, temperature, and pyrolysis time achieving different percentage yields of by-products (Balat et al., 2009). Besides, the operating condition of the process can be manipulated to obtain the specific and higher conversion of product yields. For such, the low reaction temperature with slow heating rate and prolonged pyrolysis time may favor biochar production. Bio-oil and syngas yield can be maximized with a higher heating rate and rising pyrolysis temperature.

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Biochar is carbon-rich material resulting from the pyrolysis process. The biochar product can be characterized by high carbon content, stability, and porosity. Much interest and research have focused on the development of biochar in agricultural and environmental applications. The remarkable physicochemical properties of biochar as a soil additive may enhance soil fertility and promote plant growth (Tan et al., 2021). The amendment of biochar can reduce the need for chemical fertilizer, making it a sustainable approach to improve plant nutrient cycles. Biochar also was applied as an adsorbent to remove contaminants effectively from soil or water. Production of biochar depends on the pyrolysis operating conditions and the type of feedstock used. Several factors that influence the yield and properties of the biochar include reaction temperature, pyrolysis time, carrier gas flow, and biomass material (Yang et al., 2021). Previous studies mainly focused on the effects of operation parameters on bio-oil yield from the pyrolysis of OPW (Palamanit et al., 2019). A less extensive study on biochar production from varied OPW materials has been reported. The pyrolysis of OPW must be optimized in order to achieve the maximum yield of biochar.

In this study, the biochar produced from slow pyrolysis of palm oil mill residues namely EFB, PKS, OPT, and OPF. Firstly, the response surface methodology (RSM) was used to optimize the production of biochar. The interaction among pyrolysis temperature, pyrolysis time, and N_2 gas flow rate was designed by Box-Behnken Design (BBD) experiments using EFB materials as a feedstock. Then, the correlation of influence pyrolysis parameters on biochar yield can be evaluated. The region of the optimum condition was determined through contour and 3D response surfaces plots. Subsequently, the OPW was pyrolyzed at the optimum operating condition. The produced biochar was further characterized using thermogravimetric (TGA) and scanning electron microscope (SEM) analysis.

2. Experimental

2.1 Materials

Oil palm waste of OPT, OPF and PKS were obtained from Felda Ijok, Perak while EFB sample was collected from Felda Penggiling, Johor. The collected OPW were air-dried until the moisture content reached less than 10%. Then, the residues were ground into approximately >0.5 mm particle size using the cutting mill. The grounded residues were sieved and further air-dried to remove the remaining moisture before the pyrolysis process.

2.2 Preparation and characterization of biochar

The biochar samples were prepared in a laboratory-scale quartz tube furnace reactor. For each run, 5 g of OPW sample was loaded to an alumina crucible boat and introduced into the horizontal quartz tube furnace reactor. The sample was slowly pyrolyzed at a heating rate of 10 °C/min at varied reaction temperatures (400-700 °C) and pyrolysis time (30-120 min) under N_2 flow (0.4-1 L/min) (Dai et al., 2014; Fiore et al., 2018; Yang et al., 2021). Nitrogen gas was continuously supplied inside the reactor for 30 min before the pyrolysis process to maintain the inert environment. Then, the biochar products were collected after the reactor cooled down to room temperature. The selected biochar was characterized using TGA and SEM analysis.

2.3 Experimental design

There were two pyrolysis experiments performed. Firstly, the effect of pyrolysis parameters on biochar yield was analysed by using RSM and BBD to optimize the biochar production. Based on the BBD, the total design variables and responses were generated for different parameters for biochar production. An analysis of three independent variables was carried out, including the pyrolysis temperature (X_1) of 400–700 °C, the pyrolysis time (X_2) of 30-120 min, and the N_2 flow rate (X_3) of 0.4-1 L/min. The response was taken to be the biochar yield. In total, 17 runs were designed using an EFB as feedstock. The experimental data were then fitted to second-order polynomial model as shown in Eq (1):

$$Y = B_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_i {X_i}^2 + \sum_{i} \sum_{j} B_{ij} X_i X_j \tag{1}$$

where Y is the predicted response; B_0 is a constant; B_i is the linear coefficient; B_{ij} represents the interactions of the effect; X_i and X_j are the coded value factors of the independent variables. The analysis of variance (ANOVA) was used for the statistical analysis of the model. The optimum of pyrolysis parameters also was determined through ANOVA analysis. Then, other OPW materials of OPT, OPF, and PKS were pyrolyzed at the optimum operating condition to view the effect of chemical composition on biochar production.

3. Results and discussion

3.1 Box-Behnken design and statistical analysis

The complete set of experiment and the response values using the BBD were shown in Table 1. As a result, the highest yield of 33.6 wt% of biochar was obtained at 400 °C, 30 min, and 0.6 L/min flowrate of N_2. Comparatively, minimum biochar yields of 25 wt% were obtained at 700 °C and 60-120 min of pyrolysis time under 0.4 and 1 L/min of N_2. Then, the effect of pyrolysis parameters on biochar yield were analysed using the statistical packaging software of Design Expert (Version 13.0). The yield data was successfully fitted with the second-order polynomial model as the coefficient of determination (R_2) of 0.9994, which was higher than 0.8 was obtained. For biochar production, a comparison of predicted results and the actual results were analysed. The experimental data points were close to the diagonal line. This indicates a developed model can be used to predict biochar yield within the limits of the experimental factors.

Table 1: Experimental design and responses values

Run	X_1(°C)	X_2(min)	X_3(L/min)	Y_1(wt%)
1	400	30	1.0	31.6
2	500	30	1.0	27.8
3	600	30	1.0	26.8
4	700	30	1.0	26.0
5	400	60	1.0	31.6
6	400	90	1.0	30.6
7	400	120	1.0	30.4
8	400	30	0.8	31.8
9	400	30	0.6	33.6
10	400	30	0.4	31.4
11	700	120	1.0	25.0
12	600	90	0.8	25.6
13	500	60	0.6	27.2
14	700	60	0.4	25.0
15	600	120	0.6	26.4
16	500	90	0.8	29.4
17	500	30	0.4	31.2

An analysis of the influence of the temperature, pyrolysis time and N_2 carrier gas flowrate on biochar production was conducted using a quadratic model. The response surface of biochar yields from the quadratic model was generated as depicted in Figure 1. In the analysis of the ANOVA results, three factors were found to significantly influence the yield of biochar. Biochar yield was influenced primarily by pyrolysis temperature, as depicted in Figure 1(a). As the rising pyrolysis temperature gives a lower yield of biochar. Biochar yield decreased from 33.6 wt% to 25 wt% over the temperature range of 400 to 700 °C. As the pyrolysis temperature increased, rapid decomposition of lignocellulosic components was analyzed resulting in a reduction in biochar yield (Selvarajoo and Oochit, 2020). In addition, the biochar yield also slightly decreased when the pyrolysis time increases from 30 to 120 min. These results indicate the greater primary decomposition of the EFB sample and an enhanced secondary reaction over prolonged pyrolysis time. Moreover, the effect of N_2 flowrate on biochar yield also was assessed. The highest biochar yield was produced at 0.7 L/min of N_2. Further increases in N_2 flowrate were found to reduce biochar production. As the N_2 flow increases, the pyrolysis volatile may be removed from the hot zone, which may shorten the residence time for vapors. The shorter residence time of the vapor prevented the volatile biomass components from initiating the re-polymerization process. Then, the volatiles was driven out rapidly, which lowered biochar yields (Ertaş and Hakki Alma, 2010). Overall, ANOVA analysis of operation factors determined the optimal conditions for biochar production. The optimal biochar yield (27.2 wt%) production was obtained at 550 °C, 75 min, and 0.7 L/min of N_2 flow rate.

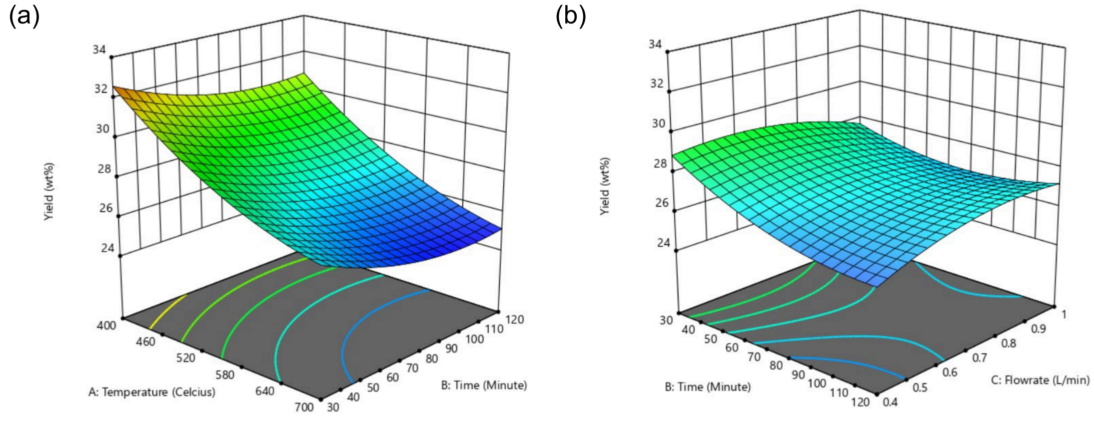

Figure 1: 3D response of: a) the effect of temperature (°C) and retention time (minutes), b) the effect of temperature (°C) and nitrogen flowrate (L/min) on the biochar yield.

The pyrolysis of EFB was conducted at the optimum pyrolysis condition to compare the percentage error between the predicted and observed values. From Table 2, it can be observed that the percentage error is below 10%. This shown the high desirability of the results can be obtained using the optimum condition suggested from ANOVA analysis.

Table 2: Optimized value of pyrolysis parameters.Parameters

	Set goal	Values	Observed	Error (%)
Temperature (° C)	In range	550		
Time (min)	In range	75		
Flowrate (L/min)	In range	0.7		
Yield (g)	Maximize	1.44	1.36	5.6

3.2 Biochar yield and characterization

The biochar yield from different types of OPW is shown in Figure 2. The result showed the different types of OPW produced a varied range of biochar yield (27-31.2 wt%) at the optimum pyrolysis condition: pyrolysis temperature of 550 °C, pyrolysis time of 70 min, 0.7 L/min of N_2 flow. The highest biochar yield of 31.2 wt% was produced from the pyrolysis process of PKS. A previous study by Promraksa and Rakmak (2020) also observed the highest yield of biochar generated from pyrolysis of PKS compared to OPF and EFB samples. The varied range of biochar yield may due to different levels of lignocellulose content OPW, particularly on lignin content. As the carbon content of biochar is mainly correlated to the lignin content of biomass. According to Khalid et al., (2019), PKS has been reported to have a lignin content as high as 50.7 wt%, while EFB, OPF, and OPT are approximately 22.1 wt%, 21.7 wt%, and 25.7 wt%. Shibata et al. (2008) also analyzed the high lignin content of PKS compared to other OPW material. A high lignin content may promote char formation and the carbonization process. Thus, a high yield of biochar was obtained from the pyrolysis of PKS.

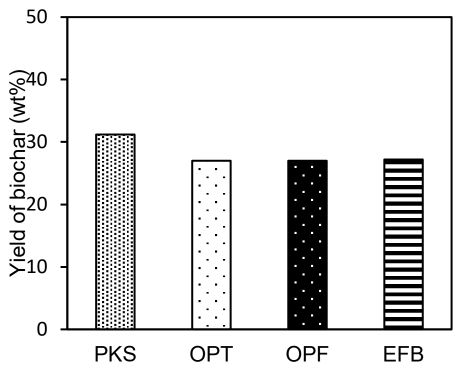

Figure 2: Biochar yield from various oil palm waste under optimum pyrolysis condition.

The thermal decomposition behavior of the oil palm biochar via thermogravimetric (TG) and differential thermogravimetric (DTG) curves shown in Figure 3. The TG profile shows three main stages of thermal degradation: drying and evaporation of light components (up to 150 °C), devolatilization of hemicellulose and cellulose (220-400 °C), and lignin decomposition (> 400 °C). The dehydration processes of pyrolyzed OPW biochar begins at 150 °C as the moisture inside the OPW sample was evaporated. Then, the decomposition of hemicellulose and cellulose starts from 150 to 450 °C. All OPW biochar shows a weight decrease from 400 to 850 °C due to the degradation of lignin constituents. The slow degradation rate of OPT was analyzed in comparison to other biochar samples. The DTG curves of OPW biochar verified the low peaks at the temperature range of 100-150 °C due to moisture reduction. The mass-loss rate of the biochar produced from OPT, OPF, and EFB has increased at a temperature of 400-450 °C. The results show that biochar with low lignin content degraded at lower temperatures The lignin decomposition for the PKS biochar occurs at a higher temperature (600-800 °C) as the peak values were observed at this temperature range. Thus, the high thermal stability of PKS was analyzed compared to another biochar sample.

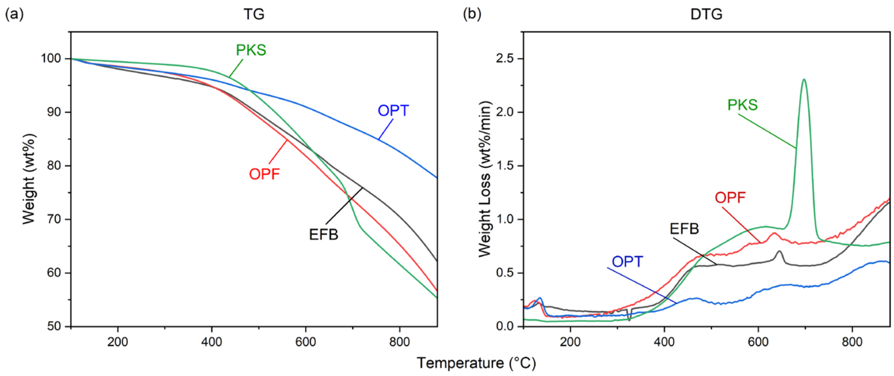

Figure 3: (a) TG and (b) DTG curves of EFB, OPT, OPF and PKS biochar.

The surface features of the biochar obtained from pyrolysis of EFB, PKS, OPT, and OPF at a pyrolysis temperature of 550 °C were perceived using SEM analysis under magnification of ×1 ,000 and shown in Figure 4. These images clearly show the porous structure of biochar. The morphology of OPF, OPT, and PKS are arranged in an orderly fashion with clearly seen pores shapes. The pore pattern at the surface resembles a honeycomb with cylindrical and polygonal pores. Only OPF and PKS biochar were observed to have clogged pores. This is similar to the findings of Mohd (2017) who analyzed the clogged pores of biochar due to the heating mechanism of the slow pyrolysis process. During the pyrolysis process, tar is deposited onto the wall of the biochar causing clogged pores. Meanwhile, an SEM micrograph of EFB biochar shows an underdeveloped pores structure. The EFB samples are incompletely pyrolyzed which causes the pores not to develop their intended structure. The influence of pyrolysis temperature and time must be extensively analyzed in order to produce well-developed porosity of biochar.

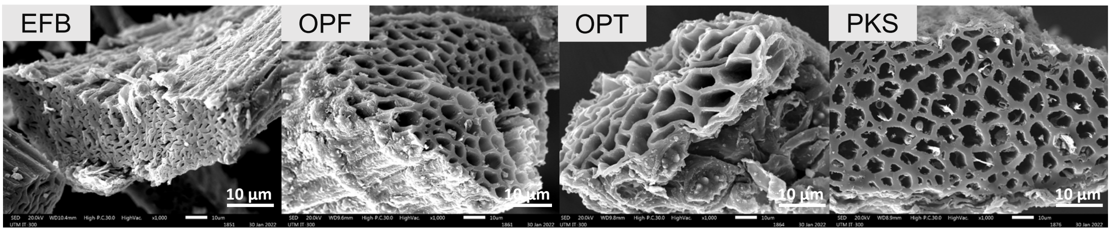

Figure 4: SEM images of biochar from pyrolysis of EFB, OPT, OPF and PKS (550 °C, 0.7 L/min, 75 min).

4. Conclusions

The yield of biochar products was dependent on the type of oil palm biomass used and the pyrolysis parameters. The results show the high pyrolysis temperature and prolonged pyrolysis time significantly reduced biochar yield. Meanwhile, the less significant N_2 flow rate effect the yield of the biochar. The optimum pyrolysis condition of biochar production was obtained through BBD and RSM analysis at 550 °C and 75 min pyrolysis time under 0.7 L/min of N_2 flow rate.

The pyrolysis of PKS provided the highest yield and thermal stability of biochar compared to other biochar samples. This may be attributed to high lignin content in PKS material. Besides, the SEM images of PKS biochar also showed a clearly seen honeycomb pore structure. PKS can be chosen as a material feedstock for biochar production since it can produce high yields and well-developed pores of biochar. However, further study needs to be conducted for the safety application of biochar particularly on polycyclic aromatic hydrocarbons (PAHs) contaminants in biochar.

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