Response surface methodology: critical parameters on the production of mangrove wood biochar yield

H Ghafar¹, R Zailani², Y Yaakob¹ and M S So’aib³

¹Faculty of Mechanical Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Malaysia.
²Faculty of Mechanical Engineering, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia.
³Faculty of Chemical Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Malaysia.

*halim4346@uitm.edu.my

Abstract. The infiltration of oxygen is unfavorable since it burned away the biomass. Other parameters were also contributed to the production of biochar. The experiments on mangrove wood were conducted using a fixed bed pyrolysis reactor with the temperature range of 300°C to 600°C, oxygen range from 0% to 10% and holding time from 2 hours to 4.4 hours. Response surface methodology (RSM) was implanted for process optimization. There were a significant effect of oxygen percentages and holding time on the production of biochar yield within the range of study. Results show that the optimum biochar yield of 15.2% when the pyrolysis temperature, oxygen percentage, and holding time were 402.5°C, 2.29% and 2 hours respectively. Confirmation experiment showed that 15.1% of biochar yield was obtained with the same pyrolysis parameters which validated the previous optimization.

1. Introduction
The dependency on fossil fuel, oil, and natural gas since more than a century ago has been a debate since the resources are non-renewable and have shown great concern over the reduction of fuel source. It was reported that more than 13500 million tonnes equivalent of oil was consumed worldwide in 2017 which equivalent to an annual growth rate of 2.2% since 2007 [1]. This shows that the dependency on these non-renewable sources is increasing. The renewable energy resources such as wind energy, solar energy, biomass energy are one of the solutions to decrease the consumption from non-renewable resources.

Mangrove forests cover about 100,000ha including peninsular Malaysia, Sabah and Sarawak [2]. There is a bright prospect for utilizing the abundant resource from mangrove wood as a raw material for the production of biochar. Oxygen infiltration is unavoidable in a mass scale of mangrove char production. The existence of oxygen during biochar production will oxidize the biochar and indirectly reduce the amount of biochar produced. This work was aimed to study the influence of oxygen percentage and other parameters; holding time and temperature on the production of mangrove wood biochar. The fact on the optimum temperature, holding time and oxygen composition to produce maximum biochar was established.
2. Materials and methods
Mangrove wood was used as a raw material in the pyrolysis of mangrove wood. The characterization of mangrove wood was also done before the pyrolysis process. The optimization process was also done aiming to maximize biochar yield percentage from the pyrolysis of mangrove wood.

2.1. Materials preparation and characterization
Mangrove wood that used as a raw material for the pyrolysis of mangrove wood was obtained from mangrove forest nearby Jalan Pandamaram, Port Klang, Selangor. The wood was cut into 1cm³ cube size before going through the drying process using oven at 60°C for about 24 hours before the experiment.

Proximate and ultimate analysis was also done in previous studies [3]. The results were shown in Table 1.

Table 1. Proximate and ultimate analysis of mangrove wood [3].

| Content                | Wt%  | Elements | 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*|
|                        |      | S        | 0.57 |

*by weight difference

2.2. Pyrolysis of mangrove wood experiment
The experiment was run in fixed bed pyrolyzer as shown in Figure 1. 5mg of mangrove wood was used in each run and stored in the airtight container before the experiment. Nitrogen gas was allowed to flow from the bottom of the reactor for more than 10 minutes before the experiment started. This was to ensure that all the air was out from the reactor. Experiments were conducted with varying gas flow containing the oxygen between 0% and 11% at a flow rate of 200ml/min, while the heating rate was set at 10K/min. The experiments were done in varied oxygen percentage, temperature and holding time as shown in the design matrix. At the end of each experiment, the char was collected and analyzed.

Figure 1. Schematic diagram of fixed bed pyrolyzer setup.
2.2.1. Design of experiment (DOE). The experimental process parameters used in this paper were oxygen percentages, temperature, and holding time. The summary of the range of the parameters is shown in Table 2. DOE software designed 20 runs as shown in Table 3.

**Table 2.** Parameters range in the pyrolysis of mangrove wood.

| Factor       | Units | Low | High |
|--------------|-------|-----|------|
| Temperature  | °C    | 400 | 560  |
| O₂ percentage| %     | 2   | 9    |
| Holding time | hour  | 2.0 | 4.4  |

**Table 3.** Design Matrix of CCD.

| Run | A: Temperature (°C) | B: Oxygen percentages (%) | C: Holding time (Hour) |
|-----|---------------------|---------------------------|------------------------|
| 1   | 400.0               | 2.3                       | 2.00                   |
| 2   | 560.0               | 2.3                       | 2.00                   |
| 3   | 400.0               | 9.0                       | 2.00                   |
| 4   | 560.0               | 9.0                       | 2.00                   |
| 5   | 400.0               | 2.3                       | 4.25                   |
| 6   | 560.0               | 2.3                       | 4.25                   |
| 7   | 400.0               | 9.0                       | 4.25                   |
| 8   | 560.0               | 9.0                       | 4.25                   |
| 9   | 345.5               | 5.6                       | 3.13                   |
| 10  | 614.5               | 5.6                       | 3.13                   |
| 11  | 480.0               | 0.0                       | 3.13                   |
| 12  | 480.0               | 11.3                      | 3.13                   |
| 13  | 480.0               | 5.6                       | 1.23                   |
| 14  | 480.0               | 5.6                       | 5.02                   |
| 15  | 480.0               | 5.6                       | 3.13                   |
| 16  | 480.0               | 5.6                       | 3.13                   |
| 17  | 480.0               | 5.6                       | 3.13                   |
| 18  | 480.0               | 5.6                       | 3.13                   |
| 19  | 480.0               | 5.6                       | 3.13                   |
| 20  | 480.0               | 5.6                       | 3.13                   |
2.3. Response surface methodology
Response surface methodology (RSM) was employed in the optimization of mangrove wood biochar produced. Central composite design (CCD) was applied for the process optimization because of its capability to analyze highly accurate design with the minimum possible number of experiments [4].

2.3.1. Analysis of variance (ANOVA). Analysis of variance (ANOVA) test was done after all the experiments done to provide significant factors in the production of mangrove wood biochar. Insignificant factors were excluded since they had no impact on the result.

3. Results and discussion

3.1. Experimental results
Mangrove wood biochar percentages for each run are shown in Table 4.

| Run | Factor A: Temperature (°C) | Factor B: Oxygen percentage (%) | Factor C: Holding times (hours) | Yield percentage (%) |
|-----|-----------------------------|---------------------------------|---------------------------------|----------------------|
| 1   | 400.0                       | 2.3                             | 2.00                            | 15.10                |
| 2   | 560.0                       | 2.3                             | 2.00                            | 9.09                 |
| 3   | 400.0                       | 9.0                             | 2.00                            | 7.54                 |
| 4   | 560.0                       | 9.0                             | 2.00                            | 16.19                |
| 5   | 400.0                       | 2.3                             | 4.25                            | 4.64                 |
| 6   | 560.0                       | 2.3                             | 4.25                            | 0.95                 |
| 7   | 400.0                       | 9.0                             | 4.25                            | 1.31                 |
| 8   | 560.0                       | 9.0                             | 4.25                            | 1.26                 |
| 9   | 345.5                       | 5.6                             | 3.13                            | 17.05                |
| 10  | 614.5                       | 5.6                             | 3.13                            | 2.25                 |
| 11  | 480.0                       | 0.0                             | 3.13                            | 22.39                |
| 12  | 480.0                       | 11.3                            | 3.13                            | 1.31                 |
| 13  | 480.0                       | 5.6                             | 1.23                            | 17.88                |
| 14  | 480.0                       | 5.6                             | 5.02                            | 1.31                 |
| 15  | 480.0                       | 5.6                             | 3.13                            | 4.49                 |
| 16  | 480.0                       | 5.6                             | 3.13                            | 1.10                 |
| 17  | 480.0                       | 5.6                             | 3.13                            | 1.06                 |
| 18  | 480.0                       | 5.6                             | 3.13                            | 1.32                 |
| 19  | 480.0                       | 5.6                             | 3.13                            | 1.44                 |
| 20  | 480.0                       | 5.6                             | 3.13                            | 1.68                 |

3.1.1. Analysis of variance (ANOVA). ANOVA analysis is shown in Table 5. The model in which the p-value < 0.05 shows the effectiveness of the model. Main factors B (oxygen percentages) and C
(holding time) was found a significant influence on the model with p-value <0.05. The model equation developed is shown in equation (1) where $Y$ is the yield percentage of biochar.

$$\frac{1}{\sqrt{Y}} = -0.79 - 1.21 \times 10^{-3} \times \text{Temperature} + 0.03 \times O_2 + 0.20 \times \text{Holding time}$$ \hspace{1cm} (1)

The value of lack of fit was 0.2923 indicated that the lack of fit was not significant relative to the pure error. Non-significant lack of fit was desirable. There were 29.23% chances that the lack of fit was due to noise error. Lack of fit error is referred to the error between model and true function[5]. The data were normally distributed as shown in the normal plot of residuals in Figure 2. The points that are closed to the reference line were considered as non-significant, while the further away points were regarded as significant [6].

| Source                  | Sum of squares | DF | Mean square | F value | Prob > F |
|-------------------------|----------------|----|-------------|---------|----------|
| Model                   | 2.67           | 2  | 1.33        | 12.58   | 0.0004   |
| B: Oxygen percentage    | 0.53           | 1  | 0.53        | 4.97    | 0.0395   |
| C: Holding time         | 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 |             |         |          |

Figure 2. Normal plot of residuals.

3.1.2. Effect of parameters on the production of mangrove wood biochar. It was found that maximum biochar can be obtained at lower oxygen percentage, lower pyrolysis temperature and shorter holding time. It was reported that high biochar yield at 400˚C whereas above 600 ˚C, gas generation such as
CO and CH₄ would be preferred [7]. The char yield decreased with the increasing of temperature. This was because most condensable volatiles was released as the degradation of hemicellulose and cellulose continue between 260°C and 360°C as previously studied [3].

While previous studies reported that longer holding time (residence time) contributed to higher char yield, the opposite trend was observed where char yield decreased with longer holding time. This was possibly due to the presence of oxygen which leads to higher oxidation of char yield when longer exposed to oxygen. A higher percentage of oxygen content during the pyrolysis of mangrove wood caused the decreased of char yield. Therefore, oxygen percentage and holding time have the most significant effect compared to temperature in the production of mangrove wood-derived biochar. Based on the linear model suggested by RSM, optimum biochar yield predicted was 15.2% when the oxygen percentage of 2.29%, the temperature was 402.5°C while holding time was 2 hours. Confirmation experiment was done with the same parameters showed that the char yield was 15.1% which was closed to the predicted char yield of 15.2%.

![Figure 3. Effect of process parameters on mangrove char yield.](image)

**4. Conclusion**
The effect of temperature was not significant compared to oxygen percentage and holding time. The presence of oxygen and holding time play an important parameter for the production of mangrove wood-derived biochar. The optimum condition of 15.2% of char yield was achieved when the oxygen
percentage was 2.29% pyrolysis temperature was 402.5°C and holding time was 2 hours. The confirmation experiments proved that 15.1% of char was achieved for the same parameters set. Thus, this validates the model. Further study suggested to be conducted on the relationship between oxygen percentage and holding time must.

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