Process optimization of microwave assisted co-pyrolysis of coal and oil palm shell blend with carbon surfaces

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Abstract. In this study, Oil Palm Shell (OPS) waste biomass and coal were subjected to Microwave (MW) co-pyrolysis conditions. The effects of process parameters on the efficiency of co-pyrolysis blended fuel were tested to identify the optimal processing conditions. The results of this study suggest that co-pyrolysis blended fuel over 35-55-75wt% carbon loading with 3-Layer method at 600W and 4LPM of N₂ flow rate suggests that increasing the carbon loading increases the oil yield. This suggests that experimental design space for carbon loading can be narrowed down. For that reason, 55wt% carbon loading was selected as the minimum and 75wt% carbon loading as the maximum range. The levels of MW selected power were 600W and 720W, where the highest is based on the maximum rated capacity of multimode MW oven (800W). The response surface methodology was used to establish model yields. The process temperature of blended fuel solids with 3-Layer method were recorded by online thermocouples and discussed. The co-pyrolysis oil obtained under various conditions were tested for chemical composition and reported.

Keywords. Oil palm shell, carbon surfaces, microwave co-pyrolysis, blend, optimization.

1. Introduction
The non-renewable crude oil, Natural Gas (NG) and coal resources still dominated as the major energy sources to power our world. These natural and finite energy resources are exploited to drive our modern societies and are at the verge of getting extinct. In addition, the dramatic energy demands in transportation, aviation and industrial power sectors of many countries have ensured increasing production from these fossil fuel resources. More importantly, fossil fuel utilization through combustion augmented CO₂, sulfur and nitrogen oxides emissions. To address the growing energy insecurity and emissions motivated scientists and researchers to explore renewable and cleaner fuel resources. Coal still remains the largest and cheapest source of solid fuel across the globe [1, 2], and is mainly used to produce electricity in Coal Power Plants (CPPs) [3]. Coal combustion offers an inexpensive energy but at the expense of some serious environmental concerns, such as CO₂, SOx, NOx, particulate matter and mercury emissions [4]. The search for cleaner energy production from coal is driving many countries to partially replace renewable waste biomass in CPPs. The motivation to use waste biomass in CPPs is growing but with some serious technical challenges, such as ignition and combustion problems (flame stability), fouling and slagging, and high temperature corrosion etc.
The second interesting option is co-pyrolyze coal with waste biomass to recover valuable fuel and energy products.

Microwave (MW) assisted pyrolysis has been demonstrated as a promising alternative to conventional pyrolysis [10-13]. The integration of MW technology to pyrolysis provides a challenging environment to treat various materials, which can improve liquid and gaseous fuel products. Several authors demonstrated that MW assisted pyrolysis offers low temperature and energy efficient route to convert biomass solids to valuable fuels [14-16]. More interestingly, MW assisted pyrolysis of biomass solids with carbon based Microwave absorber (MWA) demonstrated, improved bio-oil selectivity in terms of phenol yield [17-20], high content syngas [21, 22] and high quality bio-char [23]. Previous studies on MW assisted pyrolysis of waste biomass indicated that the process factors influencing bio-oil yield are: MWA loading [24, 25] and MW power [26]. In addition, factors that are assumed to have minimal effects on bio-oil yield can be eliminated, as well as the factors that are categorical [27]. Most MW assisted pyrolysis techniques developed previously mainly focused towards intimately mixing of MWA with pyrolysis solids [17, 20, 25, 28] with much less attention towards uniform distribution method. The use of non-uniform distribution of MWA with pyrolysis solids or intimately mixing of heterogeneous solids under MW irradiation conditions initiate hotspots phenomena, a phenomena when the MWA absorbs much higher MW energy than the surrounded pyrolysis solids and results in intense heating of MWA (commonly observed a spark). These hotspots are mainly responsible of non-uniform process heating and deteriorate pyrolysis reaction mechanism.

Further, difficulty in online temperature were noticed when thermocouple tip in contact with hotspots resulted in thermocouple meltdown. In these concerns, the distribution of MWA with pyrolysis material was paid attention to design an energy efficient system to minimize and control hotspots. We proposed and tested novel method of controlling the hotspots by surface methods, the detail of the surface method and preliminary results are discussed [29-34]. In addition, till to date, few studies were carried out to optimize fuel products from MW assisted pyrolysis of biomass solids [20, 35-39].

To the best of our knowledge, no study has been carried out to optimize co-pyrolysis products of coal and biomass blend under MW assisted pyrolysis environment in the presence of MWA and with surface methods. The primary aim of this study was to investigate the effects of uniformly distributed Coconut Activated Carbon (CAC) absorber over coal and Oil Palm Shell (OPS) blend at various levels of CAC loading, MW power and N_2 flow rate on heating profile and pyrolysis product yield. The response surface methodology was used to establish model to predict oil, blend-char and gas yields.

2. Materials and Methods

For this study, co-pyrolysis of Oil Palm Shell (OPS) and coal blended fuel arrangement was selected for the optimization study. This is based on the preliminary results and following three reasons; (i) ease of operation, (ii) better heating performance, (iii) higher oil yield compared to segregated fuel arrangement. More interesting, the preliminary results of co-pyrolysis blend over 35-55-75wt% carbon loading with 3-Layer method at 600W and 4LPM of N_2 flow rate suggested that increasing the carbon loading increases the oil yield. The oil yield was measured 24.23wt%, 28.20wt% and 31.72wt% using 35wt%, 55wt% and 75wt% carbon loading, respectively. This suggests that experimental design space for carbon loading can be narrowed down. Therefore, 55wt% carbon loading was selected as the minimum and 75wt% carbon loading as the maximum range. The levels of MW selected power were 600-720W, where the highest is based on the maximum rated capacity of MMW oven (i.e. 800W). In addition, the effect of N_2 flow rate on MW pyrolysis performance of isolated fuels suggests that the test levels for the co-pyrolysis blend is 4-8 Liters per minute (LPM) [30, 31].

With three factors, full factorial CCD experimental design with three blocks plus star was studied to investigate the significant effects on oil, blend-char and gas yield. The effects of CAC loading (X_1), MW power (X_2) and N_2 gas flow rate (X_3) was investigated at five different levels i.e. star low, low, medium, high and star high and are coded as \( -\alpha, -1, 0, +1, +\alpha \) respectively. The response surface methodology was used to establish model yields. The MW assisted co-pyrolysis experimental setup is similar to our study and can be seen in [34]. The co-pyrolysis oil obtained under various MW operating conditions was tested in GC-MS for chemical composition. The co-pyrolysis product yields were calculated using equation (1), (2) and (3).
The process temperature of blended fuel solids with 3-Layer were measured by labeling thermocouples TUML, TMML and TBMML representing upper mixed layer, middle mixed layer and bottom mixed layer, respectively. Where M in the subscript stands for mixed (i.e. blend). With three selected factors (i.e. CAC loading, MW power and N₂ flow rate), n = 3, the experimental design is required to study the possible interaction between factors and to develop response surfaces, so 2ⁿ factorial design was eliminated [40]. Moreover, 3ⁿ factorial design can be used to develop the response surfaces with 27 experiments required. However, a CCD (commonly called Box-Wilson Design) is often used instead of 3ⁿ factorials to minimize number of experiments, which can save time and expenses. Therefore, CCD was selected as suitable design for the response surface methodology (RSM) studies. For model analysis, equation (4) was used.

\[
Y_i = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} b_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} b_{ij} x_i x_j
\]

Where \( Y_i \) = Predicted response, \( x_i \)= Independent variables, \( b_0 \)= Intercept coefficient, \( b_i \)= Coefficient for linear effects, \( b_{ii} \)= Coefficient for quadratic effects, \( b_{ij} \)= Coefficient for interaction effects. This experimental design uses 9 coefficients, given by the equation (5) are used to predict the response surfaces.

\[
Y_i = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{11} x_1^2 + b_{22} x_2^2 + b_{33} x_3^2 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3
\]

Where \( Y_i \) = predicted response, i.e. oil, blend-char and gas yields. \( x_1, x_2, x_3 \)= linear effects of CAC loading, MW power and N₂ flow rate, respectively. \( x_1^2, x_2^2, x_3^2 \)= quadratic effects of CAC loading, MW power and N₂ flow rate, respectively. \( x_1 x_2, x_1 x_3, x_2 x_3 \)= Interaction effects for CAC loading-MW power, CAC loading-N₂ flow rate, MW power-N₂ flow rate, respectively. \( b_0, b_1, b_2, b_3 \)= coefficients for offset term, MWA loading, MW power and N₂ flow rate respectively. \( b_{11}, b_{22}, b_{33} \)= quadratic coefficients for the effects of CAC loading, MW power and N₂ flow rate, respectively. \( b_{12}, b_{13}, b_{23} \)= Interaction coefficients for CAC loading-MW power, CAC loading-N₂ flow rate, MW power- N₂ flow rate respectively.

STATISTICA® software was utilized to perform regression modeling for oil, blend-char and gas yield. The observed responses were entered into the program at the prescribed experimental design parameters (i.e. CAC loading, MW power and N₂ flow rate). The standard least square model was selected to run the full model as described in equation (4). The model results was analysed statistically and graphically. Initially, the deviations of actual experiment data were observed from the predicted values called residuals, which ensures that the experimental values are not interrelated to one another in some way. The overall fitness of the predicted models was checked by the \( R^2 \) value (coefficient of determination) that gives the variation in percentage. Furthermore, the significance of higher \( R^2 \) value was reviewed by F-test method using ANOVA table. A standard ANOVA table was generated using STATISTICA® software. The \( F_{ANOVA} \) is the ratio of Mean Square Regression (MSR) to the Mean Square Error (MSE). The MSE is based on degree of freedom and sum of square for regression models. The degree of freedom is the number of estimated model based parameters and observations. The standard ANOVA table is shown in Table 1.

| Source                  | Degree of Freedom | Sum of squares | Mean square | \( F_{ANOVA} \) |
|-------------------------|-------------------|----------------|-------------|-----------------|

Table 1. Standard analysis of variance table
Regression (model)  m  SSR  MSR = SSR/m  MSR/MSE
Residual error  N- m-1  SSE*  MSE=[SSE/(N- m-1)]
Total  N-1  SST=SSR+SSE*

Where, N and m represents the number of experiments and number of model parameters, respectively. The $R^2$ can be calculated using the ratio of Sum of Square Regression (SSR) and Sum of Square Total (SST), or taking the square root of MSE called Root Mean Square Error (RMSE). RMSE is an important parameter to evaluate the model, which estimates the standard deviation of residual error. The $F_{\text{ANOVA}}$ calculated from ANOVA table was compared with $F_{\text{critical}}$ value, which accounts for the degrees of freedom and desired confidence level. For this study, 95% confidence level or $p$ value $\leq 0.05$ was selected for the model coefficients. For $F_{\text{ANOVA}} > F_{\text{critical}}$, the model is considered significant at 95% confidence level. Otherwise null hypothesis is valid, which implies that the full regression model is insignificant.

The significant of each coefficient was determined using Pareto chart. A student t-distribution was used to estimate the parameter value in the model equations accounting the standard error at confidence limits, whereas the $p$-value are used to check the significance of each manipulated variables in the process. Therefore, significance of each variable on process was determined by comparing t-distribution with $p$-value. For this reason, the Pareto chart was analysed for $p$-value $\leq 0.05$ and higher student t-distribution. Moreover, the most and the least significant factor and their effects were predicted on oil, blend-char and gas yield. After statistical model analysis, several graphical representations were generated. A three-dimensional response surfaces were prepared to observe influence of multiple factors on given response by keeping other factors constant. The optimized conditions for the oil, blend-char and gas yield were determined using response surfaces. Additional experiments were conducted at optimized conditions and compared with predicted values. The optimized runs were repeated twice to verify the predicated critical value.

The co-pyrolysis oil chemical composition were analyzed using Agilent Technologies 6890 GC–MS with HP-5MS capillary column of 30 m length and 250 lm diameter. The GC oven temperature was raised from initial temperature of 80°C to 200°C at 10°C/min, and then to 300°C by 5°C/min. The final oven temperature of 300°C was held constant for about 10 min. Helium gas flow rate was maintained at 2 mL/min. The GC was connected to Agilent Technologies 5975 series Mass Spectroscopy (MS) equipped with inert Mass Selective Detector (MSD) at scanning acquisition mode. The MS conditions were: mode Electron Ionization (EI), ion source temperature 230°C, emission current 34.6l A, ionization energy 70 eV, full scan range of 50–550 and quantization by Selected Ion Monitoring (SIM) mode. The Agilent Chemstation software was used to indentify chemical compounds and peaks with the help of NIST library.

3. Results and Discussion
3.1 Microwave assisted heating behaviour

The real time heating behaviour of blended solids under various levels of carbon loading (wt%), MW power (W) and $N_2$ flow rate (LPM) is shown in Figure 1. The final pyrolysis temperature reached in blended solids is shown in Figure 2. The heating profiles indicate that the heating rate and final pyrolysis temperature reached in fuel solids are influenced by the process variables.
Figure 1. MW heating behaviour of blended solids under various MW pyrolysis operating conditions
Figure 2. Effects of process variables on maximum final pyrolysis temperature of blended solids

3.1.1 Effects of N₂ flow rate

The heating rate and final pyrolysis temperature reached in fuel solids were found to vary with N₂ flow rate. The upper fuel solids demonstrated significant increase in heating rate and final pyrolysis temperature when pyrolysis was carried out by maintaining N₂ flow rate of 4LPM at 600W and 55wt% carbon loading. However, increasing the N₂ flow to 8LPM decreased the upper fuel solids heating rate and final pyrolysis temperature. On the contrary, the heating rate and final temperature of middle and bottom fuel solids increases significantly with increasing N₂ flow rate (Figure 1 and 2, Run 1-2). The final pyrolysis temperature under these conditions were observed [T_UML=397°C, T_MML=401°C, T_BML=349°C]4LPM and [T_UML=313°C, T_MML=508°C, T_BML=436°C]8LPM. With 720W and 55wt% carbon loading produced slight increase in heating rate and final temperature of fuel solids at 8LPM compared to 4LPM (Figure 1 and 2, Run 3-4). Similarly, 600W and 75wt% carbon loading with 4LPM slightly raised the heating rate and final pyrolysis temperature of upper and bottom fuel solids compared to 8LPM. However, the middle fuel solids showed significant increase in heating rate with 4LPM, which then decreases significantly with 8LPM (Figure 1 and 2, Run 5-6). With 720W and 75wt% loading, the upper and bottom fuel solids demonstrated no significant effects on heating rate and final temperature with 4-8LPM N₂ flow rate, but middle fuel solids showed similar heating behaviour to that of 600W, 75wt% carbon loading with 4-8LPM (Figure 1 and 2, Run 7-8).

From the above discussion, it is clear that the heat generated by carbon solids and carried with N₂ flow plays an important role in controlling heat to the supported fuel solids. As carbons are good MWA and respond quickly to MW energy [11]. Therefore, MW reflected by the cavity walls is mainly absorbed by the carbon solids and converted to heat, which can then be transmitted to the supported fuel solids. As a result of high N₂ flow rate, the heat carried with inert gas is higher than the heat generated by the carbon solids, which can reduce the heating rate and final pyrolysis temperature in fuel solids. The heat carrying capacity with N₂ gas was reported to influence MW pyrolysis reaction temperature [41].

More importantly, the use of fairly low N₂ flow rate of 2.7LPM demonstrated non-uniform heating rate and significant difference in final pyrolysis temperature of fuel solids (Figure 1, Run 17), whereas increasing the N₂ flow rate to 6LPM and 9.6LPM controls the heating rate and final pyrolysis temperature of fuel solids by achieving nearly complete uniformity of process temperature (Figure 1, Run 9-14 and 18). This suggests that the heat carried with N₂ gas from carbon and fuel solids, and heat carried with N₂ gas from the MW reaction zone reached equilibrium. This important finding suggests that the uniform process heating of fuel solids in the presence of carbon surfaces can be achieved by controlling N₂ flow rate.
3.1.2 Effects of microwave power

Increasing MW power from 600W to 720W with 55wt% carbon loading and 4LPM indicated no effects on heating rate and final pyrolysis temperature of upper and bottom fuel solids. However, significant increase in heating rate and final temperature of middle fuel solids was observed with 720W (Figure 1 and 2, Run 1 and 3). With 8LPM and 75wt% loading, increasing MW power increases the heating rate of upper and middle fuel solids but remains constant for bottom fuel solids. Moreover, no significant effects on final temperature were noticed under these conditions (Figure 1 and 2, Run 2 and 4). With 75wt% and 4LPM, the heating rate and final temperature of upper and bottom fuel solids remained fairly constant with MW power but the heating rate and final temperature of middle fuel solids significantly increases with 720W (Figure 1 and 2, Run 5 and 7). With 75wt% and 8LPM, increase in MW increases the heating rate of upper and bottom fuel solids, but decreases significantly for middle fuel solids. In addition, the final pyrolysis temperature of fuel solids under these conditions was not affected with MW power (Figure 2, Run 6 and 8). Another noticeable development is the significant increase in fuel solids heating rate with 760W, 55wt% carbon loading and 6LPM (Figure 1, Run 16). Moreover, comparison of heating profiles under similar carbon loading and N2 flow rate but with 560W and 660W showed much lower heating rate of fuel solids (Figure 1, Run 15 and 9-14). However, no significant difference in final pyrolysis temperature was observed under these conditions. The higher heating rate of fuel solids is mainly the result of increase in electron intensity at higher power and increased heat generation rate from carbon solids. In addition, the synergistic effects of MW coupling with carbon absorber loading and the heat carried with inert gas can encourage fuel solid heating rate.

3.1.3 Effects of carbon loading

Comparison of heating profiles with increase in carbon loading from 55-75wt% showed no significant effects on upper fuel solids heating rate at 600W and 720W with 4LPM of N2 gas, but 55wt% showed higher heating rate of middle and bottom fuel solids, which then decreases with 75wt% loading. Moreover, the final temperature reached in fuel solids maintains much similar conditions (Figure 1 and 2, Run 1 and 5). Similar heating conditions of fuel solids were observed with 600W and 8LPM, but the middle and bottom fuel solids maintains much higher final temperature at sustained pyrolysis conditions for longer duration with 35wt%, which decreases with 75wt% loading (Figure 1, Run 2 and 6). The final pyrolysis temperature with under these conditions were observed [T_{UML}=313^\circ C, T_{MML}=508^\circ C, T_{BML}=436^\circ C]_{55wt\%}, which changes to [T_{UML}=333^\circ C, T_{MML}=426^\circ C, T_{BML}=335^\circ C]_{75wt\%} (Figure 2, Run 2 and 6). The use of 720W and 4LPM showed no effects on heating rate and final pyrolysis temperature of fuel solids (Figure 1 and 2, Run 4 and 8). However, 720W and 8LPM produced much higher heating rate of middle fuel solids with 55wt% for longer sustained pyrolysis duration, which decreases significantly at 75wt%. Moreover, final temperature conditions under these conditions were not affected with carbon loading (Figure 1 and 2, Run 4 and 8). Another noticeable development is the increase in fuel solids heating rate with 600W, 81.3wt% carbon loading and 6LPM (Figure 1, Run 20). Moreover, comparison of heating profiles under similar MW power and N2 flow rate with 48.7wt% and 55wt% showed slow heating rate of fuel solids (Figure 1, Run 19 and 9-14). In addition, the final pyrolysis temperature was observed higher for sustained longer pyrolysis duration with 81.3wt% compared to 48.3wt% and 55wt% loading (Figure 2, Run 19, 9-14 and 20). The final pyrolysis temperature under these conditions remained higher at [T_{UML}=417^\circ C, T_{MML}=414^\circ C, T_{BML}=376^\circ C]_{81.3wt\%}, which decreases to [T_{UML}=304^\circ C, T_{MML}=364^\circ C, T_{BML}=360^\circ C]_{48.7wt\%} and [T_{UML}=313^\circ C, T_{MML}=382^\circ C, T_{BML}=335^\circ C]_{55wt\%}. It is also important to note that the use of higher loading of 81.3wt% showed fairly smooth heating of fuel solids by reaching nearly complete uniformity process temperature at higher temperature for longer sustained pyrolysis condition (Figure 1, Run 20) with minimum difference in final temperature of fuel solids (Figure 2, Run 20). This suggests that the heat generated by the carbon solids at higher loading and carried with N2 gas to fuel solids can maintain sustained pyrolysis conditions for longer duration. This important finding also suggests that the uniform process heating of fuel solids can be achieved by increasing the carbon loading.

3.2 Response surface methodology
Statistical response surface methodology provides a reliable method of analyzing process conditions and interaction effects. The design of the experiment with three process variables, i.e., CAC loading (wt%), MW power (W) and N₂ flow rate (LPM) at five levels with twenty experiments are shown in Table 2.

### Table 2. Central composite design with coded values at various levels and observed responses

| DOE | Actual Run | Factors | Oil Yield (wt%) Y₁ | Blend-char Yield (wt%) Y₂ | Gas Yield (wt%) Y₃ |
|-----|------------|---------|-------------------|-------------------------|-------------------|
| 1   | 1          | CAC loading (wt%) x₁ | 55 (-1) | 600 (-1) | 4 (-1) | 28.20 | 47.47 | 24.33 |
| 2   | 4          | MW power (W) x₂ | 65 (0) | 660 (0) | 6 (0) | 31.27 | 41.04 | 27.69 |
| 3   | 6          | N₂ flow rate (LPM) x₃ | 75 (+1) | 720 (+1) | 8 (+1) | 31.36 | 41.51 | 25.35 |
| 4   | 7          | Block | 1 | 1 | 26.48 | 40.98 | 34.34 |
| 5   | 9          | | | | | 32.38 | 43.47 | 24.15 |
| 6   | 10         | | | | | 33.13 | 41.50 | 25.35 |
| 7   | 2          | | | | | 32.55 | 42.00 | 25.45 |
| 8   | 3          | | | | | 29.17 | 38.87 | 29.87 |
| 9   | 5          | | | | | 31.72 | 45.33 | 22.95 |
| 10  | 8          | | | | | 33.09 | 39.51 | 30.19 |
| 11  | 11         | | | | | 31.72 | 45.33 | 22.95 |
| 12  | 12         | | | | | 31.36 | 41.51 | 25.35 |
| 13  | 19         | | | | | 32.55 | 42.00 | 25.45 |
| 14  | 20         | | | | | 33.13 | 41.50 | 25.35 |
| 15  | 15         | | | | | 32.38 | 43.47 | 24.15 |
| 16  | 16         | | | | | 33.72 | 45.33 | 22.95 |
| 17  | 17         | | | | | 31.36 | 41.51 | 25.35 |
| 18  | 18         | | | | | 32.55 | 42.00 | 25.45 |
| 19  | 13         | | | | | 33.13 | 41.50 | 25.35 |
| 20  | 14         | | | | | 33.00 | 42.23 | 24.77 |

CCD design with three factors and 3 blocks: Standard Design Summary: 2³ cube plus star (central composite design), number of factors: 3, number of blocks: 3, number of runs: 20 [2³ = 8 (factor points, 4 cube points per factor block), 2n = 6 (6 axial points) and M = 2 (1 center point per factor block) + 1 (1 center point for axial block) + 3 (1 center point added per block)] , alpha for rotatability: 1.6818, alpha for orthogonality: 1.6733

#### 3.2.1 Model analysis

The observed responses of oil yield (Y₁), blend-char yield (Y₂) and gas yield (Y₃) responses tested for CAC loading (x₁), MW power (x₂) and N₂ flow rate (x₃) is given in Table 2. The regression coefficients of three responses are given in Table 3.

The second order polynomial model for the oil, blend-char and gas yields are given in equations (6), (7) and (8).

**Y₁** = −295.4052 + 4.3191 x₁ + 0.6718 x₂ − 11.8719 x₃ − 0.0150 x₁² − 0.003 x₂² + 0.0025 x₃² − 0.0044 x₁x₂ + 0.0010 x₁x₃ + 0.0081 x₂x₃ (6)

**Y₂** = 135.7895 − 0.7993 x₁ − 0.0923 x₂ − 7.0710 x₃ + 0.0022 x₁² − 0.00004 x₂² − 0.2067 x₃² + 0.0006 x₁x₂ + 0.0007 x₁x₃ + 0.0135 x₂x₃ (7)

**Y₃** = 259.6157 − 3.5198 x₁ − 0.5794 x₂ + 18.9429 x₃ + 0.0128 x₁² + 0.0004 x₂² + 0.2042 x₃² + 0.0038 x₁x₂ − 0.1008 x₁x₃ − 0.0216 x₂x₃ (8)
The observed and predicted value for the three responses shown in Figure 3 indicates that the experimental and predicted values are close to each other. The coefficient of determination (R²) for the oil, blend-char and gas yield model equations are 0.84977, 0.8768 and 0.90307 indicating that 84.977%, 87.68% and 90.307% of the data variability are accounted to the model equations. It also indicates that only 15.023%, 12.32% and 9.693% variations in data are not accounted by the model components.

**Table 3.** Regression coefficients for observed responses

| Regression coefficients | Oil yield (wt%) | Blend-char yield (wt%) | Gas yield (wt%) |
|-------------------------|----------------|------------------------|----------------|
| Mean/Intercept          | –295.4052      | 135.7895               | 259.6157       |
| 1. CAC loading (wt%) (L) | x₁ 4.3191      | –0.7993                | –3.5198        |
| CAC loading (wt%) (Q)   | x₁² –0.0150     | 0.0022                 | 0.0128         |
| 2. MW power (W) (L)     | x₂ 0.6718       | –0.0923                | –0.5794        |
| MW power (W) (Q)        | x₂² –0.0003     | –0.00004               | 0.0004         |
| 3. N₂ flow rate (LPM) (L)| x₃ –11.8719    | –7.0710                | 18.9429        |
| N₂ flow rate (LPM) (Q)  | x₃² 0.0025      | –0.2067                | 0.2042         |
| 1L by 2L                | x₁ x₂ –0.0044   | 0.0006                 | 0.0038         |
| 1L by 3L                | x₁ x₃ 0.1000    | 0.0007                 | –0.1008        |
| 2L by 3L                | x₂ x₃ 0.0081    | 0.0135                 | –0.0216        |

L and Q stands for linear and quadratic terms

The analyses of variance (ANOVA) for the model responses are shown Table 4. It shows that the observed models as described in equations (6), (7) and (8) gives good prediction at 95% confidence level. For all models, F_value is higher than F₀.₀₅ rejecting the null hypothesis. The student’s t-distribution and p-values of each model factor is shown in Table 5. Similarly, Pareto chart given in Figure 4 shows the significance of each model coefficient by comparing smaller p_value of ≤ 0.05 or greater t-value. The largest effects on oil yield is from interaction terms of CAC loading and MW power (x₁x₂), and CAC loading and N₂ flow rate (x₁x₃) with highest t-values (–4.48178, 3.40327) and lowest p-values (0.001176, 0.006436) at 99.999% and 99.994% significance levels, respectively. The quadratic term of CAC loading (x₁²) and MW power (x₂²) can also be regarded as significant factors on oil yield at 99.992% and 99.976% significant levels, respectively. The blend-char yield is affected largely by linear terms of MW power (x₂) and CAC loading (x₁) with highest t-values (–4.95249, –4.02487) and lowest p-values (0.000576, 0.002419) with 99.998% and 99.999% significance levels, respectively. The linear and quadratic terms of N₂ flow rate (x₃) and interaction term of MW power and N₂ flow rate (x₂x₃) with 99.993%, 95.670% and 99.449% significance levels can also be considered as significant factors on blend-char yield. The gas yield are largely influenced by linear term of MW power (x₂) and interaction terms of CAC loading and MW power (x₁x₂), CAC loading and N₂ flow rate (x₁x₃), and MW power and N₂ flow rate (x₂x₃). The t-values of x₂, x₁x₂, x₂x₃ and x₁x₃ were observed highest at 4.52116, 3.91691, –3.45929 and –4.44602 with significance levels of ≥99.387%. The quadratic terms of CAC loading (x₁²) and MW power (x₂²) and linear term of N₂ flow rate (x₃) are also regarded as significant factors on gas yield with 98.170%, 98.621% and 97.466% significance levels, respectively.
Figure 3. Coefficient of determination and observed versus predicated values, (a) oil yield (wt%), (b) blend-char yield (wt%) and (c) gas yield (wt%)

Table 4. Analysis of variance

| Source                     | Sum of squares | Degree of freedom | Mean square | F_value | F_{0.05} |
|----------------------------|----------------|-------------------|-------------|---------|----------|
| **Oil yield model**        |                |                   |             |         |          |
| Regression (SSR)           | 153.96         | 9                 | 17.11       | 6.29    | >3.02    |
| Residual error (SSE)       | 27.22          | 10                | 2.72        |         |          |
| Total (SST)                | 181.18         | 19                |             |         |          |
| **Blend-char yield model** |                |                   |             |         |          |
| Regression (SSR)           | 120.16         | 9                 | 13.35       | 7.91    | >3.02    |
| Residual error (SSE)       | 16.88          | 10                | 1.69        |         |          |
| Total (SST)                | 137.039        | 19                |             |         |          |
| **Gas yield model**        |                |                   |             |         |          |
| Regression (SSR)           | 253.11         | 9                 | 28.12       | 10.35   | >3.02    |
| Residual error (SSE)       | 27.17          | 10                | 2.72        |         |          |
| Total (SST)                | 280.28         | 19                |             |         |          |

Table 5. ANOVA for response surface quadratic models

| Factor                     | Sum of squares | Degree of freedom | Mean square | T_{value} | F_{value} | p_value | Remarks |
|----------------------------|----------------|-------------------|-------------|-----------|-----------|---------|---------|
| **Oil yield model parameters** |                |                   |             |           |           |         |         |
| x_1                        | 12.555         | 1                 | 12.5548     | 2.14778   | 4.61294   | 0.057279|         |
\[
\begin{array}{ccccccc}
& x_1 & 29.6153 & 1 & 29.61532 & -3.29861 & 10.88080 & 0.008032 & \text{Significant} \\
& x_2 & 1.0338 & 1 & 1.03385 & -0.61631 & 0.37984 & 0.551460 & \\
& x_2^2 & 19.1759 & 1 & 19.17595 & -2.65430 & 7.04533 & 0.024134 & \text{Significant} \\
& x_3 & 0.0049 & 1 & 0.00490 & 0.04242 & 0.00180 & 0.967000 & \\
& x_3^2 & 0.0013 & 1 & 0.00132 & 0.02203 & 0.00049 & 0.982859 & \\
& x_1 \cdot x_2 & 54.6709 & 1 & 54.67094 & -4.48178 & 20.08635 & 0.001176 & \text{Significant} \\
& x_1 \cdot x_3 & 32.0267 & 1 & 32.02667 & 3.43027 & 11.76674 & 0.006436 & \text{Significant} \\
& x_2 \cdot x_3 & 7.5660 & 1 & 7.56605 & 1.66727 & 2.77980 & 0.126425 & \\
\end{array}
\]

**Blend-char yield model parameters**

\[
\begin{array}{ccccccc}
& x_1 & 27.3501 & 1 & 27.35007 & -4.02487 & 16.19961 & 0.002419 & \text{Significant} \\
& x_1^2 & 0.6425 & 1 & 0.64254 & 0.61691 & 0.38058 & 0.551078 & \\
& x_2 & 41.4097 & 1 & 41.40966 & -4.95249 & 24.52719 & 0.000576 & \text{Significant} \\
& x_2^2 & 0.2851 & 1 & 0.28508 & -0.41092 & 0.16885 & 0.689800 & \\
& x_3 & 19.3420 & 1 & 19.34199 & -3.38473 & 11.45638 & 0.009649 & \text{Significant} \\
& x_3^2 & 9.0305 & 1 & 9.03053 & 5.34883 & 0.043304 & 0.974595 & \\
& x_1 \cdot x_2 & 0.8800 & 1 & 0.88002 & 0.72197 & 0.52124 & 0.486851 & \\
& x_1 \cdot x_3 & 0.0018 & 1 & 0.00180 & 0.03265 & 0.00107 & 0.974595 & \\
& x_2 \cdot x_3 & 20.9520 & 1 & 20.95202 & 3.52278 & 12.41001 & 0.005513 & \text{Significant} \\
\end{array}
\]

**Gas yield model parameters**

\[
\begin{array}{ccccccc}
& x_1 & 2.8438 & 1 & 2.84380 & 1.02314 & 1.04683 & 0.330353 & \\
& x_1^2 & 21.5334 & 1 & 21.53338 & 2.81542 & 7.92660 & 0.018304 & \text{Significant} \\
& x_2 & 55.5296 & 1 & 55.52957 & 4.52116 & 20.44086 & 0.001106 & \text{Significant} \\
& x_2^2 & 24.1372 & 1 & 24.13719 & 2.98079 & 8.88508 & 0.013789 & \text{Significant} \\
& x_3 & 18.7313 & 1 & 18.73133 & 2.62586 & 6.89515 & 0.025342 & \text{Significant} \\
& x_3^2 & 8.8134 & 1 & 8.81343 & 1.80119 & 3.24429 & 0.101854 & \\
& x_1 \cdot x_2 & 41.6785 & 1 & 41.67845 & 3.91691 & 15.34216 & 0.002881 & \text{Significant} \\
& x_1 \cdot x_3 & 32.5087 & 1 & 32.50867 & -3.45929 & 11.96669 & 0.006130 & \text{Significant} \\
& x_2 \cdot x_3 & 53.6993 & 1 & 53.69934 & -4.44602 & 19.76714 & 0.001243 & \text{Significant} \\
\end{array}
\]

Oil yield model; \(R^2=0.84977; \text{adjusted-}R^2=0.71457; \text{MS residual}=2.721796\)
Blend-char yield model; \(R^2=0.8768; \text{adjusted-}R^2=0.76592; \text{MS residual}=1.688316\)
Gas yield model; \(R^2=0.90307; \text{adjusted-}R^2=0.81584; \text{MS residual}=2.716597\)
3.2.2 Effects of variables on responses

The 3D response surfaces plotted for three factors on oil, blend-char and gas yield are shown in Figure 5. The oil yield is influenced by quadratic terms of CAC loading and MW power, interaction terms of CAC loading and MW power, and CAC loading and N2 flow rate. The oil yield increases with increasing CAC loading at low MW power but decreases with increasing CAC loading at high MW power (Figure 5, (a)). This difference in oil production with CAC loading is mainly the result of MW power on heat generated from carbons and heat carried with inert gas to controls the final temperature and pyrolysis duration of fuel solids. At low carbon loading and MW power, decrease in heat generated of carbons and heat carried with N2 gas can reduce the final temperature and pyrolysis duration resulting in incomplete pyrolysis conditions. On the contrary, increase in carbon loading increases the heat generated of carbons and heat carried with N2 gas, which can improve final temperature and pyrolysis duration supporting pyrolysis conditions to completion (Figure 1 and 2, Run 19, 9-14 and 20). The decrease in oil yield with increasing CAC loading at high MW power can be explained by higher MW absorption capacity of carbon solids and fast heat transfer to the fuel solids by maintaining quick pyrolysis conditions and higher final pyrolysis temperature, which can promote secondary phase vapor cracking. The interaction effects of CAC loading and N2 flow rate shown in Figure 5, (b) reveals that the oil yield decreases with increasing N2 flow rate at low carbon loading but increases with increasing N2 flow rate at high carbon loading. The decrease in oil yield with higher N2 flow at low carbon loading suggests that heat carried with inert gas is higher than the heat generated by carbon solids, which can reduce final pyrolysis temperature impeding pyrolysis conditions. The higher oil production with increasing N2 flow rate at high carbon loading could be the result of increased heat carrying capacity of inert gas by improving final temperature and assisting pyrolysis conditions (Figure 1 and 2, Run 17, 9-14 and 18). The interaction effects of N2 flow rate and MW
power shown in Figure 5, (c) shows that increasing the MW power from 540W to 660W at low N₂ flow rate increases the oil yield, beyond which the oil yield decreases significantly. With higher N₂ flow, increasing MW power increases the oil yield. With low MW power, increasing the N₂ flow slightly decreases the oil yield but increases with high MW power. This difference in oil production can be attributed to the synergetic effects of MW power and heat generated by carbon solids, which can affect the heat carry capacity of inert gas and simultaneous heat transfer to the fuel solids.

The blend-char yield is affected by linear terms of carbon loading, MW power and N₂ flow rate, and interaction of MW power and N₂ flow rate as shown in Figure 5, (d), (e) and (f). The blend-char yield linearly increases with decreasing MW power both at low and high carbon loading (Figure 5, (d)). This is based on the fact that lower MW power generates less heat of carbons, which is then carried with inert gas to impede solid conversion, thereby increasing blend-char yield. However, higher MW power generates more heat of carbons and higher heat carried with inert gas and simultaneous heat transfer to the fuel solids can result in pyrolysis process to completion (Figure 1 and 2, Run 15, 9-14 and 16). The blend-char yield increases with decreasing N₂ flow rate at low and high carbon loading (Figure 5, (e)). The higher blend-char yield can be associated to decrease in heat carrying capacity of inert gas and simultaneous heat transfer to fuel solids, whereas increasing the N₂ flow decreases the blend-char yield, which is mainly of increased heat carry capacity of inert gas and simultaneous heat transfer to fuel solids. The interaction effects of N₂ flow rate and MW power on blend-char yield shown in Figure 5, (f) indicate that blend-char yield decreases with increasing MW power at low N₂ flow rate but increases with increasing MW power at high N₂ flow rate. Moreover, increasing N₂ flow decreases blend-char yield at low MW power but increases at high MW power. The gas yield is influenced mainly by linear term of MW power and interaction terms of CAC loading and MW power, CAC loading and N₂ flow rate, and MW power and N₂ flow rate.

Referring to Figure 5 (g), the gas yield decreases with increasing MW power at low CAC loading but increases with increasing MW power at high CAC loading. Similar behaviour of gas production was noticed by analyzing the interaction effects of MW power and N₂ flow rate as shown in Figure 5, (i). The interaction effects of CAC loading and N₂ flow rate shown in Figure 5, (h) shows that the gas yield decrease with decreasing N₂ flow rate at low carbon loading but increases significantly with high carbon loading. Moreover, the gas yield decreases with increasing CAC loading at high N₂ flow rate but increases significantly at low N₂ flow rate. The higher gas yield can be correlated to non-uniform heating behaviour of fuel solids and significant temperature difference for longer pyrolysis duration. Referring to Figure 1, Run 7, the middle fuel solids quickly maintained pyrolysis condition at much higher heating rate and final pyrolysis temperature for longer period compared to upper and bottom fuel solids, which resulted in highest gas yield of 38.29wt% and lowest oil yield of 22.99wt% (Table 2, Actual Run 7). Similar increase in gas yield was observed with Run 2 shown in Figure 1, where the middle and bottom fuel solids maintained quick pyrolysis conditions at much higher heating rate and final temperature compared to upper fuel solids. More importantly, lowest gas yield of 22.95wt% with 31.72 wt% oil yield occurred when the fuel solids maintained fairly uniform process heating rate with minimum difference in final pyrolysis temperature (Figure 1, Run 5). At this stage, it can be suggested that differential heating nature of fuel solids in the presence of carbon absorber for extended pyrolysis duration at elevated temperature can result in increased gas production by promoting secondary phase vapor cracking.
Figure 5. 3D response surfaces; (a), (b) and (c) effects on oil yield; (d), (e) and (f) effects on blend-char yield; (g), (h) and (i) effects on gas yield

3.2.3 Optimization by response surface modeling

The developed mathematical models for oil, blend-char and gas yields were investigated to predict critical values. The quadratic mathematical model predicted that the critical process factors for oil yield are 582W, 71.38wt% CAC loading, 3.52LPM of N\textsubscript{2} flow rate, which gives 33.17wt% oil. The observed oil yield was 31.33 wt% indicating 5.52\% error between the observed and predicted values.
The critical process factors for blend-char and gas yield quadratic mathematical models are shown in Table 6 with observed and predicted values. The heating profiles under optimized process conditions are shown in Figure 6. Several experiments were performed at the critical values to verify the accuracy of the proposed models.

| Factors                        | Observed minimum (wt%) | Critical values (wt%) | Observed maximum (wt%) | Predicted critical value (wt%) | Observed value (wt%) | % Error |
|-------------------------------|------------------------|-----------------------|------------------------|-------------------------------|----------------------|---------|
| **Oil yield model**           |                         |                       |                        |                               |                      |         |
| CAC loading (wt%)             | 48.67                  | 71.38                 | 81.33                  | 33.17                         | 31.33                | 5.52    |
| MW power (W)                  | 562                    | 582                   | 758                    |                               |                      |         |
| N₂ flow rate (LPM)            | 2.7                    | 3.5                   | 9.3                    |                               |                      |         |
| **Blend-char yield model**    |                         |                       |                        |                               |                      |         |
| CAC loading (wt%)             | 48.67                  | 83.76                 | 81.33                  | 38.44                         | 36.75                | 4.41    |
| MW power (W)                  | 562                    | 767                   | 758                    |                               |                      |         |
| N₂ flow rate (LPM)            | 2.7                    | 8.1                   | 9.3                    |                               |                      |         |
| **Gas yield model**           |                         |                       |                        |                               |                      |         |
| CAC loading (wt%)             | 48.67                  | 74.48                 | 81.33                  | 30.09                         | 32.43                | 7.79    |
| MW power (W)                  | 562                    | 790                   | 758                    |                               |                      |         |
| N₂ flow rate (LPM)            | 2.7                    | 13.8                  | 9.3                    |                               |                      |         |

Figure 6. Heating profiles under optimization conditions, (a) for oil, (b) for blend-char, and (c) for gas.

3.3 Gas Chromatography-Mass Spectrometry (GC-MS) analysis of the oil

The chemical composition of the oil obtained under various MW operating conditions consisted of several groups of chemical compounds. The chemical species were classified into twelve major groups: phenol, phenolics, guaiacols, naphthalenes, benzenes, xylene, aldehydes/ketones, alkanes, alkenes, acids, alcohols and others. The main components of the oil are phenol, phenolics, guaiacols, naphthalenes and benzenes, whereas the minor includes, xylene, alkanes, alkenes, aldehydes/ketones, acids, alcohols. The composition of the oil obtained under various MW co-pyrolysis conditions by chemical groups and by chemical classification is shown in Figure 7, (a) and (b).
Figure 7. Chemical composition of the oil under various MW co-pyrolysis heating conditions, (a) by chemical groups, (b) by chemical classification.

The co-pyrolysis oil was dominated with phenol, phenolics and guaiacols chemical species consisting of 26.00-35.10%, 14.14-18.61% and 11.68-18.19% GC-MS area, respectively. The phenolics were mainly composed of 2/3-methyl phenol, 2,4/3,5-dimethyl phenol and 2/3-ethyl phenol. The guaiacols consisted mainly of 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 4-ethyl-2-methoxy-phenol, 2,6-dimethoxy-phenol, 2-methoxy-4-(1-propenyl)-phenol, 2,6-dimethoxy-4-(2-propenyl)-phenol. The naphthalenes and benzenes detected remained 3.63-7.59% and 6.30-11.07% GC-MS area, respectively. The naphthalenes were mainly composed of 1/2-methyl naphthalene and 2,6/2,7-dimethyl naphthalene. The alkanes and alkenes in the oil remained fairly low of 1.10-4.44% and 0.25-2.88% GC-MS area, respectively. It can be observed that the chemical composition of the oil under various conditions remained fairly unchanged. However, higher phenol content of 35.10% GC-MS was detected when the pyrolysis was carried out at 600W, 75wt% CAC loading and 4LPM (Figure 7,
This higher phenol production can be associated to the slow heating rate and fairly uniform process heating conditions of fuel solids (Figure 1, Run 5). More importantly, the maximum final temperature recorded under these conditions of $T_{UML}=405^\circ C$, $T_{MML}=376^\circ C$, $T_{BML}=344^\circ C$ were observed for fairly shorter pyrolysis duration, which might have reduced secondary phase vapor cracking since the pyrolysis vapor generated from upper fuel solids flows over fairly low temperature environment.

More interesting, the fuel solids showed fairly smooth heating rate and uniform process heating conditions with Run 9-14 and Run 18 as shown in Figure 1. However, phenol content under these conditions is lower than Run 5. This decrease in phenol content is mainly of the higher heating rate and final pyrolysis temperature of middle and bottom fuel solids for sustained pyrolysis conditions for longer duration. Similar uniform heating behaviour of fuel solids was also observed with Run 20 in Figure 1. However, the heating rate and final temperature reached in fuel solids under these conditions was observed higher compared to Run 5. The decrease in phenol content under most other operating conditions can be related to significant difference in heating rate and final temperature reached in fuel solids. More importantly, the higher temperature region formed in the middle and bottom of the reaction chamber as a result of non-uniformity of fuel solids can favors secondary phase vapor cracking. It is therefore suggested that uniform heating behaviour of fuel solids in the presence of carbon surfaces can minimize secondary reactions. However, the final temperature reached in fuel solids needs special attention to optimize oil for higher phenol production.

The chemical classification of the oil shown in Figure 7, (b) shows that the polars (phenol, phenolics and guaiacols) detected in fuel oil remained fairly high at 52.51-71.48% GC-MS area. The aromatics (naphthalenes, benzenes and xylene) and saturated aliphatic (alkanes and alkenes) chemical species remained 13.74-19.06% and 1.35-6.99% GC-MS area, respectively. The MW assisted co-pyrolysis of coal and OPS waste biomass with uniform distribution of carbon absorber achieved higher polar yields. This improved polar formation suggests that coal can be utilized effectively with renewable OPS biomass in MW pyrolysis system for the recovery of valuable chemicals.

4. Conclusion

This study investigated the effects of process parameters, carbon loading, MW power and N$_2$ flow rate on optimization of pyrolysis products from MW assisted co-pyrolysis of coal and OPS waste biomass blend with uniformly distributed coconut activated carbon under various operating conditions. The results showed that N$_2$ atmosphere control the fuel solids temperature, MW power influenced the fuel solid heating rate and carbon loading control the final pyrolysis temperature. The co-utilization of coal and OPS blend under MW operating conditions with carbon surfaces achieved nearly uniformity of pyrolysis heating conditions. This uniform process heating achieved either by increasing carbon loading or N$_2$ flow rate improved oil yield. In this study, uniform process heating of fuel solids with absorber medium was found essential to improve fuel conversion and selectivity. The oil was enriched in polar chemical compounds suggesting potential use as an alternative and renewable feedstock for petroleum based resins.

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