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BOX–BENKHEN DESIGN (BBD) TOWARDS OPTIMIZATION ON CO-LIQUEFACTION OF MUKAH BALINGIAN SUB-BITUMINOUS MALAYSIAN COAL AND *JATROPHA CURCAS* SEEDS

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ABSTRACT

In order to reach maximum conversion and oil yield, response surface methodology (RSM) was applied to optimize the process on co-liquefaction of Mukah Balingian coal (MB coal) and *Jatropha curcas* seed (JC seed) using 20 mL tubing reactor. Parameters involved are ratio of JC seed-to-MB coal, reaction times and temperature. The RSM based on Box-Behnken design (BBD) was employed for the optimization conditions towards conversion and oil yield. The effect of ratio, temperature and time were illustrated in perturbation plot. Based on linear term, ratio JC seed-to- MB coal with highest F-Value of 3760.08 and 1543.13 shows the greatest effect on the conversion and oil yield. There are good agreement between the actual and predicted values of conversion and oil yield. By increasing ratio of JC seeds-to-MB coal (20/80 to 80/20 ratio of JC/MB) and temperature (360 to 420 °C) with actual time of 75 min, the conversion increased from 25 to 74%. By increasing temperature (360 to 420 °C) and times (15 to 75 min) with actual 80/20 ratio of JC seeds-to-MB coal, the oil yield increased from 12 to 54%. Thus, the suggested optimum conditions for conversion were at 420 °C with 20/80 ratio of JC/MB and 75 min that reached 74% and the optimum conditions for oil yield were at 420 °C with 20/80 ratio of JC/MB and 54 min that reached 54%. Both suggested optimum conditions have desirability of 1.000.

Keywords: Co-liquefaction; sub-bituminous coal; Jatropha curcas seeds; response surface methodology; conversion; oil yield

INTRODUCTION

Co-liquefaction of coal with biomass has become hot topic to be discussed in order to increase the yield of liquefaction products and it shown by previous studies that the appearing of positive synergetic effect in the co-liquefaction of coal with biomass[1]. Co-liquefaction of coal and biomass can help to enhance quality and quantity of liquefaction products and reduce cost of oil from direct coal liquefaction [2, 3, 4]. There are a lot of previous studies on co-liquefaction of coal and biomass were conducted such as rice straw, sawdust, seaweed, coconut husk and rubber seed [5, 6].

Response surface methodology (RSM) was a useful tool for developing, improving, and optimizing a process. Sadeghi-Kiakhani [7] was claimed that by using RSM, the important factors were tested simultaneously with a minimum number of trials according to individual experimental designs based on factorial designs. RSM is preferred to be used compared to traditional method since the number of experimental test can be minimized. Thus, advantage can be required by using RSM method such as ease experimental work, save time, reduce cost and environmental friendly due to reducing in chemical usage. Moreover, RSM can also be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions.

The main purpose of this study is to determine the optimum condition for conversion and oil yield obtained from co-liquefaction of Mukah Balingian coal and *Jatropha curcas* seed that is not yet explored using response surface methodology. Thus, this abundant biomass source i.e. *Jatropha curcas* seeds is highly potential candidate to be investigated for biofuel production via co- liquefaction process and development of technology becomes significant to utilize the resource efficiently, improvement of ecological environment and also for chemical feed-stock production.

EXPERIMENTAL

Materials.
MukahBalingian coal (Malaysian sub-bituminous coal) originating from Sarawak and *Jatropha curcas* was used in this study. Both samples were dried overnight at oven temperature of 45 °C. Then, were crushed and sieved to obtain particle sizes of 212 µm (MB coal) and 2 mm (JC seeds), respectively. Tetrahydrofuran (THF) (analytical reagent), *n*-hexane (industrial grade) and toluene (industrial grade) were all purchased from local supplier and all solvents used are pure chemical reagents.

Liquefaction and product fractionation.
Individual and co-liquefaction were conducted in a 20 mL tubing reactor shaken vertically. 1.0g of dried coal or *Jatropha curcas* seed or mixtures of both samples with different ratio was loaded into the reactor for each experimental run. After the process is completed, the liquefied mixture was separated by Soxhlet solvent extraction with tetrahydrofuran (THF), n-hexane and toluene.The *n*-hexane insoluble are subsequently separated into methyl benzene soluble (asphaltenes (AS)) and methyl benzene insoluble fractions, then the methyl benzene insoluble fractions will be separated into tetrahydrofuran (THF) soluble (preasphaltenes (PA)) and THF insoluble (residue) fractions. The conversion of feedstock is defined as the THF soluble fraction + gas.

Experimental design and optimization.
The Box–Behnken design (BBD) consists of a set of points lying at the midpoint of each edge and the replicated centre point of a multidimensional cube [8, 9]. The

number of experiments (N) required for the development of BBD was defined as $N = 2k(k - 1) + C_0$ (where k *was* the number of factors and C_0 was the number of central points). With three factors, the BBD model by default consists of 12 factorial design runs and 3 replicates at the central point, which mean a total of experiments is 17 runs [10]. A to C were the coded values of independent variables [8]. Based on our preliminary studies and the literatures of single-factor experiments, ratio (A), temperature (B), and time (C) were selected as the three important independent variables. The minimum point, middle point and maximum point in the selective range of respective variable was coded as −1, 0, and +1, which was given in Table 1.

Table 1
The Box–Behnken design of independent variables for optimization process.

Coded	Actual		
	A	*B*	*C*
-1.00	20.00	360.00	15.00
0.00	50.00	390.00	45.00
1.00	80.00	420.00	75.00

A= ratio (g), *B* = temperature (°C), *C* = time (min)

RESULTS AND DISCUSSION

In the batch experiments, the importance of parameters involved such as ratio, temperature and time in co-liquefaction of MB coal and JC seeds were analyzed using RSM Design-Expert 6.0.10 software. The data of the experimental result and predicted result was compared in order to check the reliability of the proposed model. For further investigation, adequacy of the proposed model was examined by using analysis of variance (ANOVA) in order to determine the significant of the main of variable on the response value [11, 12, 13]. Then, the actual result obtained was plotted in perturbation plot.

Analysis of variance (ANOVA) of the response surface quadratic model for conversion and oil yield.

The Model F-value of 525.17 (conversion) and 234.03 (oil yield) implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of “Prob> F” less than 0.0500 indicate model terms are significant. Based on linear term of ratio JC seed–to–MB coal (A) with F-Value of 3760.08 (conversion) and 1543.13 (oil yield) shows the greatest effect in co-liquefaction compare to temperature (B) and time (C) which similar with the literature [14, 15, 16]. Table 2a shows the results for the analysis of variance (ANOVA) of the response surface quadratic model terms of conversion. In this case A, B, C, B^2, C^2 are significant model terms. Table 2b shows the results for the analysis of variance (ANOVA) of the response surface quadratic model terms of oil yield. In this case A, B, C, B^2, C^2 are significant model terms. In order to improve the model, the reduction of insignificant model term is needed. The values (Prob> F) greater than 0.1000 indicate the model term are insignificant, thus it were being removed [8].

Table 2a
Analysis of variance (ANOVA) for response surface reduced quadratic model of conversion on co-liquefaction of MB coal and JC seeds.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remarks
Model	2067.20	9	229.69	525.17	<0.0001	Significant
A	1644.51	1	1644.51	3760.08	<0.0001	Significant
B	210.84	1	210.84	482.08	<0.0001	Significant
C	175.88	1	175.88	402.13	<0.0001	Significant
B^2	13.64	1	13.64	31.19	0.0008	Significant
C^2	22.18	1	22.18	50.71	0.0002	Significant

Table 2b
Analysis of variance (ANOVA) for response surface reduced quadratic model of oil yield on co-liquefaction of MB coal and JC seeds.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remarks
Model	1585.56	9	176.17	234.03	<0.0001	Significant
A	1161.62	1	1161.62	1543.13	<0.0001	Significant
B	179.27	1	179.27	238.14	<0.0001	Significant
C	71.10	1	71.10	94.46	<0.0001	Significant
A^2	26.00	1	26.00	34.54	0.0006	Significant
C^2	136.20	1	136.20	180.93	<0.0001	Significant

There was a good agreement between the actual and predicted values of conversion and oil yield in co-liquefaction of MB coal and JC seeds, which indicated the goodness of fit and reliability of the model. The high value of the coefficient of determination conversion (R^2= 0.9985) and oil yield (R^2= 0.9967) , and value of Pred R-Squared of 0.9763 and 0.9470 was in reasonable agreement with Adj R-Squared of 0.9966 and 0.9924 indicates that the chosen of quadratic model was appropriate in assuming the response value of the experimental data [17]. Figure 1a and 1b illustrated the comparison between the actual and predicted values of conversion and oil yield in co-liquefaction of MB coal and JC seeds.

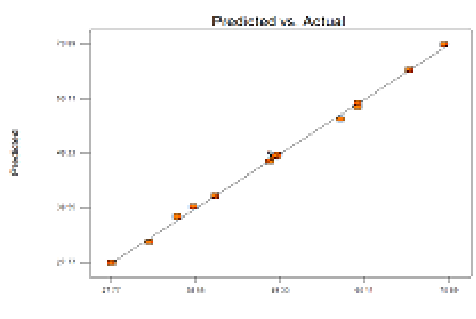

Figure 1a. Relationship between the actual and predicted values of conversion in co-liquefaction of MB coal and JC seeds.

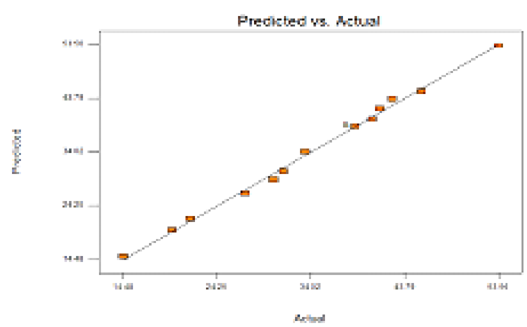

Figure 1b. Relationship between the actual and predicted values of oil yield in co-liquefaction of MB coal and JC seeds.

Perturbation plot.
Perturbation plot is graph used to determine all the factors at minimum, middle and maximum point and each variable was coded as −1, 0, and +1 [15]. Other factors are

held constants while one factor was varied in range. Thus, Figures 2a and 2b show the effect of each factor on conversion and oil yield in co-liquefaction.

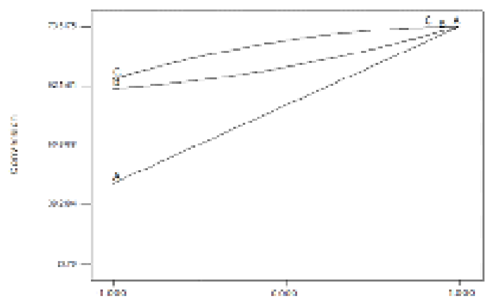

Figure 2a. Perturbation plot showing effect of ratio JC seeds- to- MB coal (A), temperature (B) and time (C) on conversion in co-liquefaction

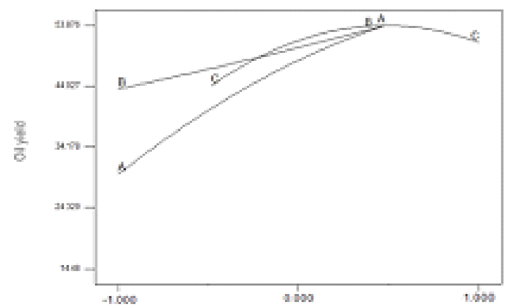

Figure 2b. Perturbation plot showing effect of ratio JC seeds- to- MB coal (A), temperature (B) and time (C) on oil yield in co-liquefaction

Ratio, temperature and time are important factor that contribute to the conversion in co-liquefaction [5, 18]. Based on figure 2a, the highest conversion reached about 74% by increase the ratio JC seeds- to- MB coal from 20 to 80%, temperature from 360 to 420 °C and time from 15 to 75 min. However each parameter has no interaction to each other. Figure 2b also shows that no interactions with the oil yield reach about 54%. Based on previous studies, temperature and ratio give major contribution on co-liquefaction process [1,5,18]. While reaction time is defined as optimum time used at pointed temperature, where the reactions time affect on co-liquefaction process by controlling mass transfer [19]. Figure 2b show that by increase the reaction time (C), the oil yield increase but when it reached certain time the oil yield start to drop. Longer liquefaction time is not beneficial for the co-liquefaction process [20] where Shui*et al.* [2] explained this reaction in following reaction mechanism:

JC seeds (JC) ® free radicals or intermediates (I_1) ® product (P_1) (1) MB coal (MB) ® free radicals or intermediates (I_2) ® product (P_2) (2) MB + I_1 ® product (P_3) (3)

This reaction was take place at reaction (3) when I_1 dependent on time and increase the oil yield. However at the certain time when I_1 reach maximum concentration, the oil yields start to drop. Thus the oil yields increase with increase in concentration of I_1 and drop when I_1 reach it maximum concentration.

CONCLUSION

The optimization of co-liquefaction of MB coal and JC seeds were successfully obtained. The conversion and yield of oil and gas in co-liquefaction of MB coal and JC seeds was investigated by optimizing three parameters namely ratio of JC seed-to-MB coal, temperature and time. The RSM based BBD was employed for the optimization process. There are 10 solutions are provided and the suggested optimum conditions for conversion were at 420 °C with 20/80 ratio of JC/MB and 75 min that reached 74% and the optimum conditions for oil yield were at 420 °C with 20/80 ratio of JC/MB and 54 min that reached 54%. Both suggested optimum conditions have desirability of 1.000.

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