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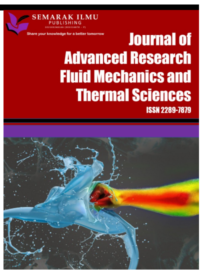

Optimisation of Ester Content in Liquefaction of Rubber Seed

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ABSTRACT

Increasing in population in the world and demand in energy has led to the depletion of fossil fuels. Renewable energy as alternative resources has intensified in recent years. Hydrothermal liquefaction is utilized in this research to convert the biomass feedstock into bio-oil. The bio-oil sample from the hydrothermal liquefaction is analysed using Gas Chromatography Mass Spectometry. A Box Behnken Design with three factors is adopted to optimise the preparation parameters in terms of reaction temperature, volume of solvent used and reaction time. From the analysis, the optimised bio-oil yield of 35.76% can be obtained from temperature of 277.20^{o}C, volume of solvent of 28.88ml as well as reaction time of 48.10 minutes. On the other hand, an ester content of 95.43% can be obtained under temperature of 265.29oC, volume of solvent of 29.95ml as well as reaction time of 47.10 minutes.

1. Introduction

With the awareness towards green energies and clean fuel are increasing rapidly at this era, the researches regarding these clean technologies are getting more concerns and attentions. Renewable energy play an vital role in sustaining energy to the vast pool of populations in developing countries without access to clean energy [1]. Among all variety of renewable energy sources, the use of biomass is the most convincing choice, as it can be transformed into liquid, solid and gaseous products. There are five categories of biomass resources: wood waste, agricultural wastes, municipal solid wastes, food waste and animal wastes, industrial wastes, energy crops grown for energy application purpose [2].

There are basically two categories of biomass conversion technologies, which are biochemical and thermo-chemical conversion. Thermo-chemical conversion (TCC) is more rapid and conducted at higher temperature under the presence of suitable catalysts in order to get liquid products from several sources. TCC can be further divided into a few main categories, which include gasification, combustion, pyrolysis, supercritical fluid extraction and hydrothermal liquefaction (HTL) [3]. HTL is a method which is carried out under a high temperature and high-pressure environment to allow the solid biomass to have sufficient time to break down into liquid components. The reactions that happens during HTL process are decomposition of particles and repolymerization. Agricultural wastes

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as biomass feedstock generally possess high content of organic constituents (lignin particles, hemicellulose, cellulose and other organics in small amount). Agricultural waste also contains high energy content [4].

Rubber seed amounts obtained in high amount from the by-product of Hevea brasiliensis, which is cultured for the latex content. Before the rubber seed is discovered for its rich content of oil, it was originally used as a planting material. Researchers later find out about the commercial value of rubber seed oil and its potential as a feedstock biomass in renewable energy source, as it can be the alternate energy source and be utilized as biodiesel.

Table 1
Properties of rubber seed oil in comparison with diesel

Property	Rubber seed oil	Diesel
Specific gravity	0.91	0.835
Viscosity (mm2/s)	76.4	7.50
Flash point (oC)	198	50
Calorific value (kJ/kg)	37500	4225
Saponification value	206	-
Iodine value	135.3	38.3
Acid value	53.0	0.062

Gas chromatographic mass spectrometry is the most crucial equipment to identify and determine the quantity of volatile and semi-volatile compounds present in the complex mixtures. GC-MS is also very useful in determining the molecular weights, as well as the compositions of elements in the organic compounds of the unknown mixtures.

Design of Experiment (DoE) is a collection of mathematical techniques which are being applied to the statistical modelling and systematic analysis of a problem, where desired responses or output will be optimized by input factors or variables. Response surface methodology (RSM) is one of the various model building in DoE. Through the design of experiments, the purpose is to optimize an output variable (response) which is affected by a few input variables (independent variables).The benefit of RSM is to decrease the number of trials needed in an experiment to study and identify the interactions between multiple variables [5]. Box–Behnken designs (BBD) is invented by George E. P. Box and Donald Behnken in 1960. This design was proposed by using only 3 levels of each variables, while having suitable number of experimental points.BBD is less time consuming, economical and efficient as it only requires 3 levels of each factor, which will result is less experimental runs to test multiple variables and the interactions between them [6]. BBD is usually believed to be an efficient and ideal alternative compared to CCD. This is due to the reason that CCD requires more experiments runs, more time and higher costs to build the model equation [7].

2. Methodology

2.1 Rubber Seed Pretreatment

The rubber seed collected from the estate is dried at oven at 110°C for 24 hours to remove any impurities and moisture content in the seed. The seed will then be crushed into smaller particles for the liquefaction process.

2.2 Experiment Data Sample

There are 17 experimental runs obtained from the Box-Behnken Design from DoE software. Surface area was optimized by studying three of the manipulated variables at different levels which are -1, 0 and +1. The parameters that will be tested are reaction time (30 minutes, 45 minutes and 60 minutes), temperature (240 °C, 270 °C and 300 °C), and the dosage of concentration of methanol (20 ml, 25 ml and 30 ml). When the liquefaction process is complete, the products that can be obtained are mainly biocrude, gaseous products and char. The mixture was recovered by using appropriate amount of DCM (dichloromethane). The DCM phase was then separated and filtered. The solvent is then evaporated to obtain the final product which is the biocrude [8].

2.3 Rubber Seed Characterisation

After obtaining the biocrude products from the hydrothermal liquefaction process, the samples will then be analysed using the gas chromatography-mass spectrometry (GC-MS). There will be 17 vials of samples be prepared, each containing 1.5ml of sample. The element compositions of the sample will be detected and identified from the results. From there, the optimum content of ester can be identified.

2.4 Optimization of Preparation Parameters

The optimization of the parameters is carried out using the BBD. After all the experimental runs has been carried out, the data will be keyed into the software to carry out optimization process.

3. Results

3.1 Bio-Oil Yield

3.1.1 RSM Optimization of Bio-oil Yield

After carrying out all the experimental runs, from the Sequential Model Sum of Square, it is suggested that the model of quadratic vs 2FI model has the highest F-value among all the other models. The F-value is 15.96. This model also has the lowest p-value, which is 0.0016. In the lack of fit tests, quadratic model also displays the lowest F value which is 0.24. This implied that the experiment was fitting the quadratic model. The selection of model is based on the highest F-value in the sequential model sum of square, and the lowest F-value in the lack of fit tests.

The analyzed results for all the 17 responses were tested using ANOVA and tabulated in the above table. The Model F-value of 9.42 implies that the model is significant. Prob<F with values less than 0.05 also show that the significant model term. There is 0.37% of chance that a “Model F-value” this big amount could occur because of noise. In this research, based on the p-value of the quadratic model, it can be concluded that the individual main effects terms (A and B) and two of the quadratic effect (A2) is significant model terms. Values larger than 0.1 indicate that the not significance in model term. Therefore, it can be concluded that the model factors (A, B and A2) have positively contributed to the model equation.

Lack of fit test can make comparison between the residual error and the pure error from replication, and thus gives F values for all the models. From the aspect of Lack-of-fit test, the number of 0.14 indicates that the not significance in Lack of Fit relative to the pure error. A chance of 93.11% that a “Lack of fit F-value this big amount could happen because of noise. A not significant lack of fit results is a desirable result to obtain an acceptable model.

Table 2
Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F-value	p-value Prob>F	
Model	317.80	9	35.31	7.38	0.0076	significant
A - Temperature	31.40	1	31.40	6.57	0.0374	significant
B - Vol of solvent	41.86	1	41.86	8.75	0.0212	significant
C – Reaction time	4.37	1	4.37	0.91	0.3712	
AB	7.37	1	7.37	1.54	0.2544	
AC	1.12	1	1.12	0.23	0.6427	
BC	2.71	1	2.71	0.57	0.4765	
A^2	159.25	1	159.25	33.30	0.0007	significant
B^2	12.78	1	12.78	2.67	0.1461	
C^2	39.30	1	39.30	8.22	0.0241	significant
Residual	33.48	7	4.78			
Lack of Fit	5.14	3	1.71	0.24	0.8634	not significant
Pure Error	28.34	4	7.08			
Correlation Total	351.28	16				

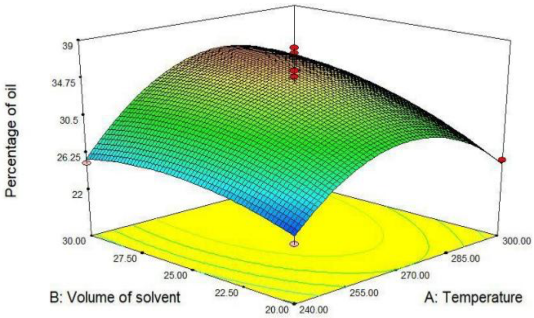

Fig. 1. 3D-plot of yield percentage with the interact effect of reaction temperature and volume of solvent used.

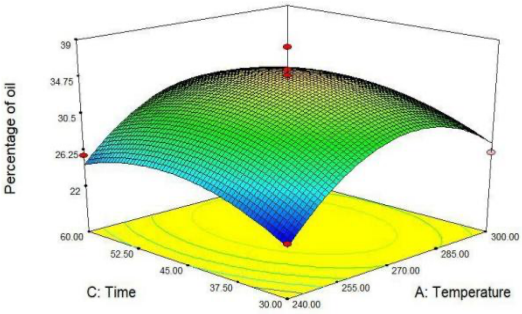

Fig. 2. 3D-plot of yield percentage with the interact effect of reaction temperature and time.

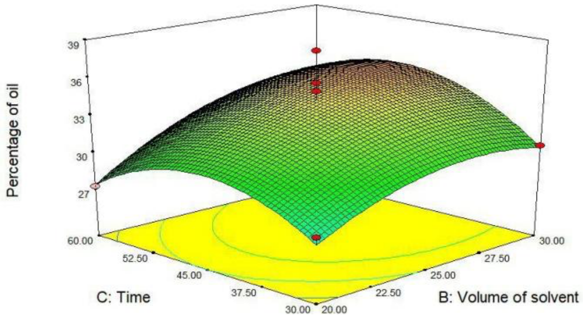

Fig. 3. 3D-plot of yield percentage with the interact effect of volume of solvent used and reaction time

Temperature is considered as one of the operating parameters that governing the hydrothermal liquefaction of biomass. Temperature can strongly cause an effect in the bio-oil yield and the properties [3]. In other research, it is also proven that the higher the reaction temperature, the higher the yield of bio-oil. This situation, however, is limited by the further increasement in temperature. This statement is explained by a few studies. Zhong and Wei [9]studied about the HTL of four different woods. They have found out that with the increasing reaction temperature, the biooil yield will increase. This is then followed by the decrease in yield when the reaction temperature further increase [9]. In this research, the highest yield of biocrude obtained was at the reaction temperature of 270°C, while the lowest yield was obtained at temperature of 240°C. According to Zhu *et al.* [10], his research on the HTL of barley straw with different reaction temperatures have achieve a conclusion. The low temperature has aided with the degradation of biomass into bio-oil. On the other way round, the higher temperature reduce the yield of bio-oil. This is due to the molecular polymerization and depolymerization [10].

From Figure 1, the effect of operating temperature shows greater effect to the bio-oil yield than that of effect of the volume of solvent used. This implies that the yield of bio-oil depended more on the temperature than the volume of solvent used.

The reaction time of the liquefaction can be interpreted as the period when the desired temperature for liquefaction is reached and maintained. The period for heating and cooling process is not accounted for. The length of the reaction time affect the yield of bio-oil in the way that shorter period of time may cause the polymerization and incomplete degradation reactions, whereas the longer period of time might leads to the polymerization of intermediate and thus reducing the bio-oil yield [11].

From previous studies, it is observed that there is no optimum reaction time for the liquefaction process. The parameters depended more on the reaction temperature, type of catalysts used and type of feedstocks. Yip et al. has studied about the liquefaction of bamboo. They have made a conclusion that the optimum reaction time for this process is 840 min after running the experiments with different range of time which are 120, 360, 600, 840 and 1080 minutes [12]. Ye *et al.* [13] carried out liquefaction of bamboo shoot shell and identified that the optimum reaction time is 80 minutes.

From Figure 2, the effect of operating temperature has greater effect to the bio-oil production than that of effect of the reaction time. This implies that the yield of bio-oil rely more on the temperature than the reaction time.

The hydrothermal liquefaction of biomass has depended greatly on the use of solvents. The use of solvents can affect the bio-oil yield, as well as the distribution of liquid products. There are several types of solvents for liquefaction process, which include supercritical fluids, water and organic solvents. Among all, the use of organic solvent such as methanol and ethanol has more advantageous compared to water. This is due to the lower critical points of alcohols than water, as well as the lower dielectric constant and boiling point compared to water [3].

From Figure 3, it is shown that when the volume of solvents used increased, the yield of bio-oil has increased along with reaction time. However, the effect is not as greater as then reaction time prolonged. This can be explained by maller ratio of biomass-to-water ratio restrict hydrolysis of the lignocellulosic solids, rendering smaller aqueous soluble products' yield and solid residue. Higher volume of solvent promote the dehydration of the aqueous products, leading to increase in the bio-oil yield.

3.1.2 Optimum reaction condition

The optimized values that obtained from the DOE software, which are using temperature of 277.20^{o}C, volume of solvent of 28.99ml and lastly the reaction time of 48.10 minutes. From the software, these optimized values will give a bio-oil yield of 35.76%. These parameters are needed to be reconfirmed by repeating the liquefaction process for 3 times according to the suggested parameter value and determine the percentage of bio-oil yield from the GCMS result. Next, the average percentage of bio-oil yield from the experimental result are compared with the predicted value of DOE software and the value of standard error need to be calculated. If the value of standard error less than 10%, then the predicted value from the software is acceptable.

$$Average\ percentage\ of\ bio-oil\ yield = \frac{34.14+33.26+34.98}{3} \tag{1}$$
$$= 34.13\%$$

$$Standard\ Error\ (SE) = \frac{Optimized\ value - Experimental\ value}{Optimized\ value} \text{ x } 100\% \tag{2}$$
$$= \frac{35.76-34.13}{35.76} \text{x}100\%$$
$$= 4.56\%$$

The value of standard error is 4.56% which is lower than 10%. Hence, the value of parameters suggested from the Box-Behnken design of DOE software can be accepted for maximum yield of bio-oil. However, if the value of standard error is less than 5 %, the result obtained considered to be high quality. Therefore, the optimized value obtained by analyzing the result to achieve maximum yield of bio-oil is considered to have high accuracy.

3.2 Ester Content

3.2.1 RSM Optimization of Ester Content

From the Sequential Model Sum of Square, it is suggested that the model of quadratic vs 2FI model has the highest F-value among all the other models. The F-value is 14.86. This model also has the lowest p-value, which is 0.0020. In the lack of fit tests, quadratic model also display the lowest F value which is 0.14. This implied that the experiment was fitting the quadratic model. The selection of model is based on the highest F-value in the sequential model sum of square, and the lowest F-value in the lack of fit tests.

Table 3
Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F-value	p-value Prob>F	
Model	180.89	9	20.10	9.42	0.0037	significant
A - Temperature	31.92	1	31.92	14.97	0.0061	significant
B - Vol of solvent	37.11	1	37.11	17.40	0.0042	significant
C – Reaction time	3.82	1	3.82	1.79	0.2225	
AB	6.71	1	6.71	3.15	0.1194	
AC	1.51	1	1.51	0.71	0.4275	
BC	4.77	1	4.77	2.24	0.1783	

A^2	83.37	1	83.77	39.09	0.0004	significant
B^2	8.58	1	8.58	4.02	0.0849	
C^2	0.63	1	0.63	0.30	0.6028	significant
Residual	14.93	7	2.13			14.93
Lack of Fit	1.42	3	0.47	0.14	0.9311	1.42
Pure Error	13.51	4	3.38			13.51
Correlation Total	195.82	16				195.82

The analyzed results for all the 17 responses were tested using ANOVA and tabulated in the following table 4.5. The Model F-value of 9.42 implies that the model is significant. Prob<F with values less than 0.05 also show that the significant model term. There is 0.37% of chance that a "Model F-value" this big amount could occur because of noise. In this research, based on the p-value of the quadratic model, it can be concluded that the individual main effects terms (A and B) and two of the quadratic effect (A2) is significant model terms. Values larger than 0.1 indicate that the not significance in model term. Therefore, it can be concluded that the model factors (A, B and A2) have positively contributed to the model equation.

Lack of fit test can make comparison between the residual error and the pure error from replication, and thus gives F values for all the models. From the aspect of Lack-of-fit test, the number of 0.14 indicates that the not significance in Lack of Fit relative to the pure error. A chance of 93.11% that a "Lack of fit F-value this big amount could happen because of noise. A not significant lack of fit results is a desirable result to obtain an acceptable model.

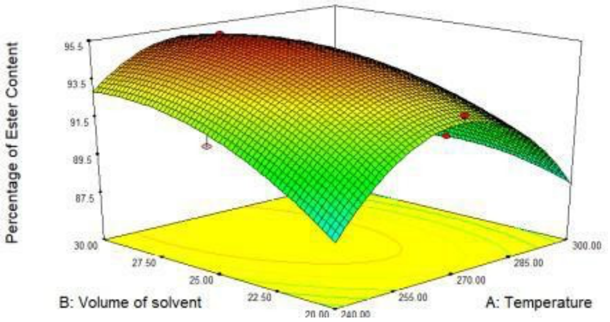

Fig. 4. 3D-plot of ester content with the interact effect of reaction temperature and volume of solvent used.

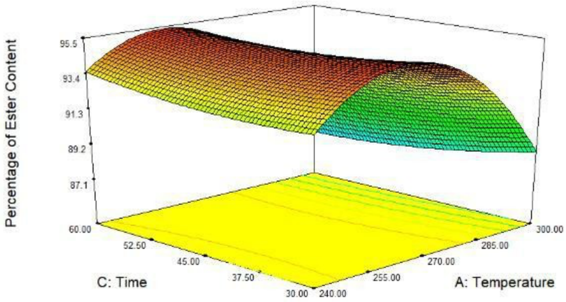

Fig. 5. 3D-plot of ester content with the interact effect of reaction temperature and time.

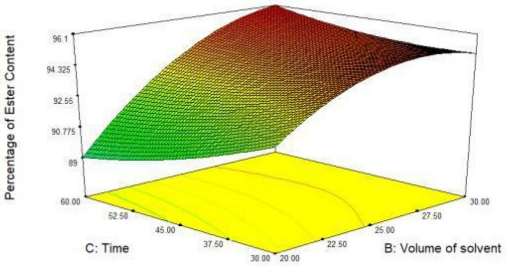

Fig. 6. 3D-plot of ester content with the interact effect of volume of solvent used and reaction time

Figure 4 shows the effect of the reaction temperature and the volume of solvent used. From the graph, it is shown that when the temperature increase, there is an increment in the ester content in the bio-oil, until the optimum temperature of around 270^{o}C, then is followed by the decrement when the temperature is further increased. Temperature is one of the most crucial parameters that will affect ester content in the bio-oil produced. This can be explained by the quick dispersion of alcohol, methanol in this case, in the liquefaction of rubber seed. There is also believed to have the reduction in the viscosity in the rubber seed when the temperature is increased [14].

Figure 5 shows the effect of the reaction temperature and time to the ester content in the production of bio-oil. From the graph, it implies that the reaction time is relatively insignificant effect on the ester content in the bio-oil production compared to the reaction temperature. The percentage of ester content remains the same as the time increase from 30 minutes to 60 minutes. According to Zhu *et al.* [15], the ester content in the biocrude oil is derived from the decomposition of the hemicellulose and cellulose composition that are contained in the biomass. The hemicellulose component is composed of a variety of sugars, which include xylose, lactose and glucose. The branch chains in the hemicellulose components make the crystallinity of the hemicellulose weaker than cellulose. Therefore, the hemicellulose can be hydrolysed easily [11].

From figure 6, the volume of solvent has significant effect on the ester content in bio-oil. When Ye *et al*. [13] did their research on the liquefaction of bamboo shoot shell, they discover that different ratio of solvent used will affect the liquefaction percentage. When the ratio of the solvent to the increased from 1:1 to 1:3, the liquefaction percentage increased from 95.83% to 99.79% [13].

In this research, the ester content in bio-oil increased when the volume of solvent used increased. The increment in percentage halt as until the ratio of 1:6, which is from 85.21% to 95.46%. This can be explained by the dehydration of the intermediate products due to the high ratio of solvent used, which lead to the high percentage of bio-oil yield and therefore high percentage of ester content [16].

3.2.2 Optimum reaction condition

The optimized values that obtained from the DOE software, which are using temperature of 265.29^{o}C, volume of solvent of 29.95ml and lastly the reaction time of 47.10 minutes. From the software, these optimized values will give a bio-oil yield of 95.43%. These parameters are needed to be reconfirmed by repeating the liquefaction process for 3 times according to the suggested parameter value and determine the percentage of bio-oil yield from the GCMS result. Next, the average percentage of bio-oil yield from the experimental result are compared with the predicted value of DOE software and the value of standard error need to be calculated.

$$Average\ percentage\ of\ bio-oil\ yield = \frac{90.59+89.21+91.85}{3} = 90.55\% \quad (3)$$

$$Standard\ Error\ (SE) = \frac{Optimized\ value - Experimental\ value}{Optimized\ value} \text{ x } 100\% = \frac{95.43-90.55}{95.43} \text{x}100\% = 5.11\% \quad (4)$$

The value of standard error is 5.11% which is lower than 10%. Hence, the value of parameters suggested from the Box-Behnken design of DOE software can be accepted for maximum yield of bio-oil. However, if the value of standard error is higher than 5 %, the result obtained considered to be less high quality. Therefore, the optimized value obtained by analyzing the result to achieve maximum yield of bio-oil is considered to have average accuracy.

4. Conclusions

For both set of experiments, quadratic models was lastly established to correlate all the three parameters to the responses, which are the bio-oil yield and the ester content in oil. Throughout the analysis of the response surface quadratic model, the parameter that shows the most significant effect on the response (biocrude oil) is the reaction temperature. This is followed by the reaction time. The volume of solvent used in each experimental runs has the least significant effect on the production of bio-oil yield. The RSM optimization results shows that a biocrude oil of 35.76% can be obtained under the optimum temperature which are temperature of 277.20^{o}C, volume of solvent of 28.99ml and lastly the reaction time of 48.10 minutes. For the ester content, the reaction temperature also shows the greatest effect on the percentage of ester in the biocrude oil. This is then followed by the volume of solvent used. The parameter that has the least significant effect on the percentage of ester content in the biocrude oil is the reaction time. From the optimization results, an ester percentage of 95.43% can be obtained with the parameters of temperature of 265.29^{o}C, volume of solvent of 29.95ml and lastly the reaction time of 47.10 minutes. For both the bio-oil yield and ester content, the highest yield and highest percentage of ester was obtained at temperature of 270^{o}C, using 25 ml of solvents and 45 minutes of reaction time.

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