Reaktor

p-ISSN 0852 – 0798
e-ISSN 2407 – 5973

Acredited: SK No.: 60/E/KPT/2016
Website : http://ejournal.undip.ac.id/index.php/reaktor/

Reaktor, Vol. 20 No. 1, March Year 2020, pp. 1-9

Optimization of Bio-oil Production from Empty Palm Fruit Bunches by Pyrolysis using Response Surface Methodology

Tutuk Djoko Kusworo*), Bayu Aji Pratama, and Dhea Putri Savira

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University
Jl. Prof. Soedarto, SH, Tembalang, Semarang, Indonesia 50275

*) Corresponding author: tdkusworo@che.undip.ac.id

(Received : September 30, 2019; Accepted: December 11, 2019)

Abstract

The need for fuel oil continues to increase in line with the increasing number of human populations and the growth rate of dependence on fuel oil. Bio-oil is a condensed-liquid mixture that results from the thermal derivation of biomass containing hemicellulose, lignin, and cellulose. This research developed an optimization of the operation condition of bio-oil from empty palm fruit bunches (OPEFB) using a modified pyrolysis reactor. The temperature and mass of empty palm fruit bunches were the two parameters considered in this study. Optimization was carried out on process parameters using the surface response methodology (RSM) and variance analysis (ANOVA). The significance of the different parameters and the effect of the relationship between parameters on the bio-oil yield is determined using a full factorial central composite design. The optimal operation condition of pyrolysis was found to be 570.71 ºC, and the mass of empty palm fruit bunch 420.71 gr. Predictions from the optimum variable of operating conditions produce a bio-oil yield of 5.58%. The actual bio-oil yield on the optimum condition that was be validated is 5.6 %. The chemical composition of bio-oil obtained was evaluated by GCMS to ensure its characterization as a fuel.

Keywords: *Empty palm fruit bunches, Bio-oil, Pyrolysis, Response Surface Methodology, Optimization*

How to Cite This Article: Kusworo, T.D., Pratama, B.A., and Savira, D.P. (2020), Optimization of Bio-oil Production from Empty Palm Fruit Bunches by Pyrolysis using Response Surface Methodology, Reaktor, 20(1), 1-9, http://dx.doi.org/10.14710/reaktor.20.01.1-9.

INTRODUCTION

The energy crisis becomes a major issue in several countries of the world, especially Indonesia. It is a problem that must be addressed right away because it can cause some economic sectors to be disrupted. The issue of the energy crisis, which becomes a current concern of the government and the world, is the scarcity of fuel oil. The demand for fuel oil continues to increase in line with the increasing number of human populations and the growth rate of dependence on fuel oil. The average consumption level for oil fuels has increased by 2.73 percent per year.

Meanwhile, according to the Ministry of Energy and Mineral Resources, crude oil reserves from fossils will run out within 22 years. The economic impact of dependence on fossil fuel can also be felt as the price of fossil fuels rises exponentially with time. It prompted many countries to develop renewable energy sources such as bio-oil (Gashaw *et.al.*, 2015). Therefore, it is necessary to diversify energy from renewable materials, such as bio-oil. Bio-oil is a condensed-liquid mixture that results from the thermal derivation of biomass containing hemicellulose, lignin, and cellulose.

Many studies have been carried out to obtain alternative raw materials that can be widely expanded as raw material (biomass) for making bio-oil. Among them are husks, straw, the pulp (pulp), tobacco, and bamboo. Energy derived from biomass can be obtained in two ways; biological (fermentation and anaerobic digestion) and thermochemical (gasification, liquefaction, and pyrolysis) processes (Wang *et.al.*, 2010). Pyrolysis is a thermochemical conversion that generates mainly liquid (bio-oil), bio-char, and gas as worth byproducts. The function of bio-oil can alternate fuel oil or diesel in many applications, such as furnaces, boilers, engines, and turbines to generate electricity (Crocker, 2010). The biomass material for making bio-oil can be obtained from one of the wastes of the plantation sector, which is very large in scale in Indonesia, namely oil palm plants. Palm Oil is one of the vegetable oil-producing plants in the form of Crude Plam Oil (CPO), which is widely planted in plantations in Indonesia, especially on the islands of Sumatera, Kalimantan, Sulawesi, and Papua. OPEFB waste is a large amount of solid waste produced, which is around 126,317.54 tons/year (Thangalazhy-Gopakumar, 2018). Bio-oil is generally made by cracking long-chain hydrocarbon molecules into short-chain hydrocarbon molecules without involving oxygen or commonly referred to as pyrolysis reactions, but also through liquefaction.

Pyrolysis can be defined as the decomposition of organic material with the help of heat (thermal) in an inert atmosphere (without oxygen), becoming a simpler compound (Biswas *et.al.*, 2017). The pyrolysis is a series of complex reactions that are influenced by several parameters such as temperature, heating rate, residence time, and feed composition Azizi *et.al.*, 2017). Pyrolysis is a thermochemical process that is generally operated at atmospheric pressure and a temperature interval between 300 ℃ to more than 700℃ with no oxygen present. The main products of pyrolysis can be solid (carbon), liquid (oil), and gas (pyro gas) with different ratios depending on operating conditions, reactor type, and raw material characteristics. Oil and carbon are the main products produced from the pyrolysis stage, while non-condensable gases are used as heat sources (Chiaramonti *et.al.*, 2015). Loh (2017) conducted a study on the manufacture of bio-oil from empty palm fruit bunches (EPFB) through the pyrolysis with a temperature range between 400-600 ℃. By evaluating the optimum parameters for bio-oil yield, it was found that the optimum temperature for the production of bio-oil is 500 ℃ with the yield of bio-oil produced reaching 30% wt. In addition, Biswas *et.al.* (2018) conducted a research on making bio-oil with raw materials of rice straw using a slow pyrolysis under the influence of CO_2 gas with thermo-gravimetric analysis method which obtained optimum operating conditions for making bio-oil from rice straw at an operating temperature of 400 ^oC yielding bio-oil is 34.5 wt%. OPEFB has been pyrolyzed in a fluidized bed system reactor, the maximum yield for liquids was obtained approximately 55%, depending on size chunk ash content, at the temperature of 450 °C and residence time of 1.03 s (Abdullah *et.al.*, 2011). However, this study has not involved a statistical approach optimization in obtaining the process parameters of bio-oil production.

Therefore, in this study, the process of making bio-oil from empty palm fruit bunches (EPFB) will be developed using a non-catalyst pyrolysis method. In the study of the pyrolysis of empty palm fruit bunch (EPFB) into bio-oil, the influential variables observed were operating temperature and mass of empty palm fruit bunches (EPFB), which would then be optimized by using response surface methodology to obtain the maximum yield of bio-oil.

MATERIALS AND METHODS

Materials

The material used in the research is oil palm empty fruit bunch (OPEFB). OPEFB is a solid waste generated from palm oil agro-industry. The OPEFB was obtained from RTC Pertamina, Ltd., Indonesia. Industrial grade nitrogen gas purity >99% was purchased from Aneka Gas, Ltd., Indonesia. All experimental results presented in this paper are on a dry basis.

Experimental Procedures

The study of pyrolysis was performed in a pyrolysis reactor. The reactor made of stainless steel and was heated by electrical heating to provide an isothermal condition for the reaction. The experiments were performed to study the optimum process parameters of pyrolysis temperature in the range 358-600°C and the mass of the sample in the range of 200-500 grams.

The experimental variables with two different parameters are defined using statistical software that integrates Response Surface Methodology. The two-process parameters in this experiment are operating temperature and mass of empty palm fruit bunches. The yield of bio-oil for the sequence of factors is predicted from the response surface method. Based on the predicted results, the parameter condition for maximum yield bio-oil is defined. An experimental variable is executed at the predicted condition to validate the predicted yield bio-oil. The components of bio-oil that is obtained at the optimum reaction condition are also determined.

Fig. 1 explains a schematic diagram of the experimental procedure used that was used. The pyrolysis reactor and feed gas (nitrogen) were heated electrically. The temperature of the pyrolysis reactor was regulated using a PID temperature controller. The reactor was adequate to heat up to 700 °C that was used to evade vapor condensation in the product gas

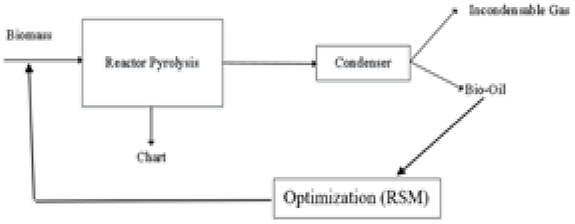

Figure 1. Schematic diagram of slow pyrolysis

stream tube. The condensable gas (bio-oil) of the pyrolysis vapor was accumulated utilizing a series of condensers that performed at low temperatures (Neto *et.al.*, 2019).

This research will be conducted in 4 stages: the preparation stage, operation phase, analysis phase, and optimization phase. The first stage of making bio-oil from empty palm fruit bunches by the pyrolysis is carried out by the preparation of the pyrolysis reactor includes the reactor’s manufacture. The next stage is a pyrolysis operation on a modified pyrolysis reactor, which starts with insert the empty palm fruit bunches into the pyrolysis reactor for the thermal cracking process with a certain mass and temperature according to the specified variables. Then the reactor streamed by nitrogen gas with a certain flowrate. The purpose of draining the nitrogen into the pyrolysis reactor is to remove the oxygen gas present in the reactor. If there is a presence of oxygen gas in the pyrolysis reactor, it will cause the formation of ash in the pyrolysis reactor and will cause the failure of the process so that the results obtained are less than optimal. The pyrolysis produces a liquid product from the bottom side and gas product from the upper side. The liquid produced from the pyrolysis is calculated as the yield tested to determine the variables that affect. Further analysis of bio-oil results done by Gas Chromatography-Mass Spectrometry (GC-MS) test for the liquid product, which aims to identify the liquid composition of pyrolysis reaction result and percentage for each type of compound contained in pyrolysis products. The final procedure is the optimization of the optimum condition to producing Bio-oil from empty palm fruit bunches by the pyrolysis with response surface methodology. Pyrolysis Reactor Equipment Set can be seen in Fig 2.

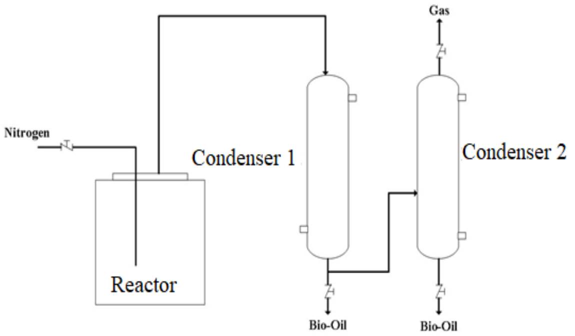

Figure 2. Pyrolysis Reactor Equipment Set

These following Eq. 1, 2, and 3 were used to calculate the yield of bio-oil, char and also gas, which is produced by each variable,

$$Y_{oil} = \frac{W_{oil}}{W_{feed}} x100\% \tag{1}$$

$$Y_{char} = \frac{W_{char}}{W_{feed}} x100\% \tag{2}$$

$$Y_{gasl} = 100\% - Y_{oil} - Y_{char} \tag{3}$$

Bio-oil Characterization using GCMS

Analysis of GCMS or Gas Chromatography-Mass Spectrometry is performed to ensure that structural changes have occurred in the oil, and to know the various types of compounds contained in the pyrolysis product sample precisely, in the presence of this analysis can be known percentage of each type of compound contained in pyrolysis products. The bio-oil recognition and composition definition were executed on a GC Agilent 6890 with Agilent mass selective detector of series 5973. Chromatographic parameters were as follows: feed volume of 0.2 µL, heated at 40°C (1 min) 6°C min^{-1} up to 300°C (10/Min) separate mode with a ratio of 100:1 and injection temperature of 290°C. The residence time was 73.3 minutes, He (helium) as bearer gas with a flow rate of 2.9 mL min^{-1} (Shah *et.al.*, 2016).

Design of experiment

The experimental design chosen for this research is Central Composite Design (CCD), and the response calculated, which is the dependent variable, is the yield of bio-oil. The step to optimize the process variables for bio-oil production from empty palm fruit bunches by pyrolysis, check the combined effect of the two different independent variables; reactor temperature and mass of empty palm fruit bunches on yield and obtain a model, two factors central composite factorial design (CCD) which contains 2^2 = 4 factorial points plus 4 center points and 2 star points prominent to a total of 10 experiments was used in this research. The response selected was the yield bio-oils gained from the pyrolysis of empty palm fruit bunches. The following Eq. 4 determined the coded values of the process variables.

$$X_i = \frac{x - x_i}{\Delta x} \tag{4}$$

Where X_i is a coded value of an ith variable, x_i is an un-coded value of the ith test variable, Δx – the difference between the measured values and x is an un-coded value of the ith test variable at the core point. Table 1 indicates the independent factors and their appropriate actual values; Table 2 shows the design matrix. The regression analysis was executed to

Table 1. Independent variables and their levels for central composite design

Independent variable		Levels				
		-1.41	-1	0	1	1.41
Temperature, °C	x_1	358	400	500	600	641
Mass, g	x_2	208	250	350	450	491

Table 2. Central composite design arrangement (experimental design matrix)

Run	Temperature (ºC)		Feed mass (g)	
	Code	Value	Code	Value
1	-1	400	-1	250
2	-1	400	1	450
3	1	600	-1	250
4	1	600	1	450
5	0	500	0	350
6	-1.41	358	0	350
7	1.41	641	0	350
8	0	500	-1.41	208
9	0	500	1.41	491
10	0	500	0	350

assume the response function as a second-order polynomial, as shown in Eq. 5.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1, i<j}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \quad (5)$$

Where Y is the predicted response, and β_i, β_{ii}, and β_{ij} are coefficients assumed from regression. They indicate the linear, quadratic, and interactions of the independent variables on the response.

RESULTS AND DISCUSSION

The Effect of Reaction Temperature on the Product Yield

The pyrolysis of empty palm fruit bunch into a bio-oil will be divided into three phases of yield; there are gas, liquid, and char. In this study, the influence of various variables towards the yield of bio-oil and bio-char has been observed. One of the variables that have been studied is temperature. On the constant mass of 350 g empty palm fruit bunch used, the correlation between temperature and bio-oil & bio-char yield is stated in the following Fig.3

Based on Fig. 3, it is known that temperature has an opposite effect between the bio-oil yield and biochar yield. In bio-oil, there is a rise in yield along with the increase of the pyrolysis reactor's temperature used. Meanwhile, in bio-char, there is a decrease of yield along with the increase of the pyrolysis reactor's temperature used.

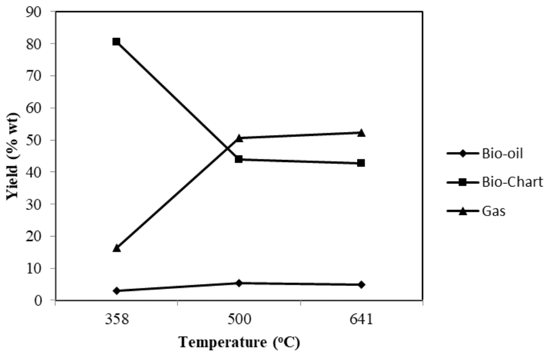

Figure 3. The yield of Pyrolysis Products at Various Pyrolysis Temperature with Biomass of Empty Palm Oil Bunches and Mass of 350 gram

In bio-oil yield, the higher the temperature of the pyrolysis reactor used, the greater the percentage of bio-oil produced. The function of temperature in the pyrolysis is to provide the heat needed to decompose bonds in biomass. The efficiency of biomass conversion will increase with increasing temperature; this is due to the additional energy to break the chemical bonds in the biomass (Guedes *et.al.*, 2017). The higher the pyrolysis temperature will result in a higher heating rate. A high heating rate limits the effect of mass transfer and higher lignin degradation so that it will cause more oil to be produced (Sembiring *et.al.*, 2015). However, the yield of bio-oil produced reaches its maximum point at 500 °C, which is 5.3%.

In comparison to the data presented by Chan *et.al.* (2014), the yield of bio-oil is lower in work here showed. The possible explanation is that when the reactor temperature used increases to a temperature of 600 °C, the yield of bio-oil obtained decreases to 5%. It is due to the temperature at 600 °C, a secondary decomposition reaction of the volatile liquid fraction occurs, which produces pyrolysis vapor, which cannot be condensed (Chan *et.al.*, 2014).

While for bio-char yield, it occurs the opposite phenomenon with bio-oil yield. The higher the temperature of the pyrolysis reactor, the smaller the percentage of biochar produced. When the reactor temperature gets higher, the heating rate will also be higher. Rapid heating will lead to the depolymerization process of solid materials into volatile compounds so that the bio-char yield will decrease (Sembiring *et.al.*, 2015).

The Effect of Empty Palm Fruit Bunch's Mass on Product Yield

In addition to temperature, the mass of raw materials is also a variable that affects the pyrolysis of biomass. In this study, several variations of the mass of OPEFB were used. At a constant temperature of 500 ºC, the relationship between the mass of OPEFB and the yield of bio-oil, bio-char, and gas produced is stated in Fig. 4.

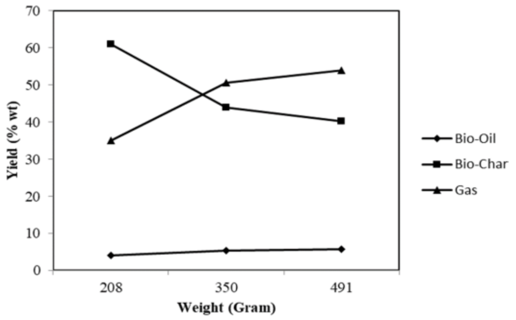

Figure 4. The yield of Pyrolysis Products at Various Biomass Mass with Biomass of Empty Palm Oil Bunches and Temperature of 500 ^oC

Based on Fig. 4, the pyrolysis products yield varies with variation of feed mass. Different response is shown by each product. For gas and bio-oil products, the increase of feed mass significantly increases the yield, however the solid residue decreases from 60% to 40%.

In bio-oil yield, the mass of empty palm fruit bunches has a significant influence on the distribution of products. The more OPEFBs used, the higher the yield of bio-oil produced. If the mass of empty palm fruit bunches used is high, there will be more condensed steam formed. It will cause the vapor residence time in the pyrolysis reactor to be reduced, thus preventing a secondary cracking reaction and causing the bio-oil yield to increase (Guedes *et.al.*, 2018).

Meanwhile, for bio-char yield, the mass of the empty palm fruit bunch has the opposite effect compared to the impact on bio-oil yield. Heat transfer occurs faster in the smaller mass of empty palm fruit bunches, which will then lead to faster devolatilization and cause the formation of organic gases and vapors. However, due to the low generation of a gas phase at a lower feed mass, the residence time of a volatile compound will be longer. In other words, the interaction between volatile solids will take longer, leading to the re-polymerization of volatile compounds and causing more numbers of char to form on small mass variables (Amin *et.al.*, 2011).

The more OPOPEFB used, the less bio-char yield will be produced. If there are more empty palm fruit bunches used, then there will be less steam time. It causes the secondary fracturing of steam to gas and re-polymerization to form secondary char not going well, so the bio-char yield will decrease (Guedes *et.al.*, 2017).

Data Collection of Production of Bio-Oil Yield from Empty Palm Fruit Bunch

The relationship between process variables and the yield of bio-oil produced was analyzed using a central composite design (CCD) model. The second-order polynomial regression equation is obtained from the relationship between the response of bio-oil yield (Y) and the process variable: reactor temperature (X_1), the mass of palm bunches (X_2). The bio-oil yield of the research results is presented in Table 3.

Table 3. The Result of Bio-oil Yield from Observation and Prediction

Run	X_1	X_2	Y	$Y_{predicted}$	Residue	Error (%)
1	-1	-1	3.2	3.08	0.12	3.7
2	-1	1	4.2	4.33	-0.13	3
3	1	-1	4.8	4.74	0.06	1
4	1	1	5.2	5.39	-0.19	3.5
5	0	0	5.3	5.30	0.00	0
6	-1.41	0	3.0	3.00	-0.00	0.06
7	1.41	0	5.0	4.92	0.08	1.4
8	0	-1.41	4.0	4.14	-0.14	3.3
9	0	1.41	5.7	5.48	0.22	3.8
10	0	0	5.3	5.30	0.00	0

Analysis of Variance (ANOVA) and Regression Model Evaluation for Bio-oil Production from Empty Palm Fruit Bunch

The relationship between process variables and the yield of bio-oil produced was analyzed using a central composite design (CCD) model. The second-order polynomial regression equation is obtained from the relationship between the response of bio-oil yield (Y) and the process variable: reactor temperature (X_1), the mass of palm bunches (X_2). The result of the ANOVA method for the regression model equation, significance test value, and regression coefficient are presented in Table 4.

Based on Table 4, the results of ANOVA show the equation of the model that can be used to analyze the results of the study. The second-order polynomial model equations for yield responses are as follows:

$$\textbf{Yield oil} = -22.0868 + 0.0789X_1 + 0.0293X_2 - 6.687 \times 10^{-5}X_1^2 - 1.5 \times 10^{-5}X_1X_2 - 2.44 \times 10^{-5}X_2^2 \qquad (6)$$

The significance of the regression coefficients is evaluated based on p-values and F-value to extend a regression model. The variables are significant if the p-value is lower than 0.05, and an F-value is higher than 4.46. From Table 4.2, it is found that X_1, X_1^2, X_2^2 are significant factors. X_2 variable is included in the model since it has a p-value lower than 0.05; however it has an important role with an indication of F-value more than 4.46. Based on the statistical analysis, the interaction between X_1 and X_2 factors is not significant. It shows that the temperature and feed mass are independently influencing the product of pyrolysis.

Table 4. Analysis of Variance (ANOVA)

Factor	Coeff	SS	Df	MS	F	P-Value
Model	-22.09		5			0.0024
X_1	0.08	3.68	1	3.68	102.45	0.0005
X_1^2	$-6.69*10^{-5}$	2.04	1	2.04	56.86	0.0017
X_2^2	$-2.44*10^{-5}$	1.81	1	1.81	50.31	0.0021
X_2	0.03	0.27	1	0.27	7.55	0.0514
X_1X_2	$-1.5*10^{-5}$	0.09	1	0.09	2.50	0.1887
Residue		0.14	4	0.04		
Total SS		7.78	9	3.68	102.45	0.0005
Std dev 0.929814796, R^2 = 0.98152, Adj R^2= 0.95841						

The regression equation model after the insignificant variable is omitted becomes:

$$\mathbf{Y = -22.0868 + 0.0789X_1 + 0.0293X_2 - 6.687*10^{-5}X_1^2 - 2.44*10^{-5}X_2^2} \quad (7)$$

Significance analysis shows that the polynomial model has a high significance because the value of the p-value is 0.0023911 or less than 0.05. The significance of the variable showed in Table 5.

Table 5 shows that the variables of temperature and mass of empty fruit palm oil bunches are significant because of the F-value higher than F-table. The value of the determination coefficient (R^2) is 0.98152, and adj R^2 is 0.95841. It shows that the model explains 98.15% variation in the research data, and variables outside the operating variable influence only 1.85%.

Response Surface of Bio-oil Production from Empty Palm Fruit Bunch

The interaction between process variables with bio-oil yield can be studied through plotting the three-dimensional curve of the independent variable while placing other variables at the center position (point 0). The 3D curve of the response (yield bio-oil) with other variables (Temperature and mass) is shown in Fig. 5.

Table 5. Result of F-value and F-table

Factors	F	F table
X_1	102.4502	
X_1^2	56.8636	
X_2^2	50.3133	4.46
X_2	7.5543	
X_1X_2	2.5032	

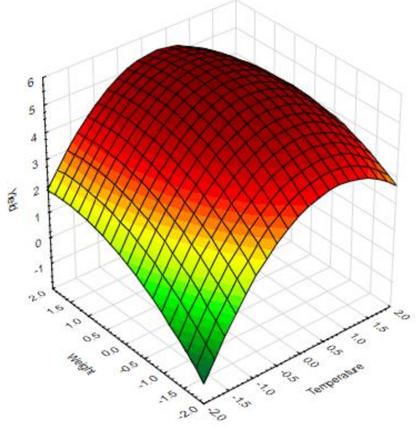

Figure 5. Interaction between temperature and mass of empty palm fruit bunch towards bio-oil and bio-char yield

The response surface curve is used to determine the optimum conditions of each independent variable to produce maximum yield. The elliptical response surface curve indicates that there is good interaction between the two variables, and circular curves indicate no interaction between the two variables (Onukwuli *et.al.*, 2017). Fig. 5 shows the interaction between two variables. The optimum condition can also be obtained from the plotting response surface. The coordinates at the center with the highest contour level are the optimum point positions. The optimum point of operating conditions can be evaluated through critical points in Table 6 and the desirability index in Fig 6.

Table 6. Critical Point of Optimum Variables

Factor	Observed Minimum	Critical Values	Observed Maximum
Temperature (ºC)	358.58	541.21	641.42
Mass (gr)	208.58	434.86	491.42

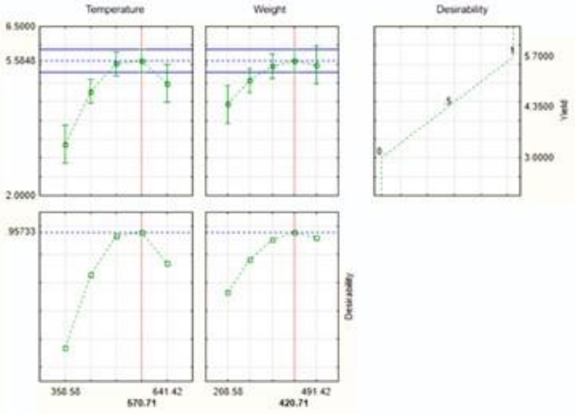

Figure 6. Index Desirability of Variables

Table 7. Value of yield Bio-oil RSM Prediction and Experiment

	T (^{0}C)	Mass (gr)	Yield (%)
Predicted	570.71	420.71	5.58
Experiment	571	420.71	5.6
Error			0.3

In Fig. 6, it can be seen that the optimum conditions for the formation of bio-oil from empty palm fruit bunches through the pyrolysis occur with the highest value desirability of variables. The optimum conditions are temperatures of 570.71 ^{o}C and the mass of empty palm fruit bunch 420.71 gr.

Predictions from the optimum variable operating conditions produce a bio-oil yield of 5.58%. The experiments were executed at these optimum conditions to approve the portend optimum values. This optimized condition was approved with the real bio-oil yield in 5.6 %. The temperature of the reaction in the process of forming bio-oil through the pyrolysis has a significant role. The temperature in the pyrolysis has the function to supply the heat required to decompose bonds in biomass. The efficiency of biomass conversion will increase with rising the temperature; this is caused the additional energy to break down the chemical bonds in the biomass (Guedes *et.al.*, 2017). The higher the pyrolysis temperature will result in a higher heating rate. A high heating rate limits the effect of mass transfer and higher lignin degradation so that it will cause more oil to be produced (Sembiring *et.al.*, 2015). But the bio-oil yield will decrease above the temperature of 600 ^{o}C. This result is due to at 600 ° C; a secondary decomposition reaction of the volatile liquid fraction occurs, which produces pyrolysis vapor, which cannot be condensed (Chang, 2014).

Bio-oil Characterisation

Gas Chromatography-Mass Spectrometry analysis is carried out to determine the content of organic components in the pyrolysis liquid products. Figure 6 showed the peak of chemical compound with the support of Table 6, which lists the possible compounds of empty palm oil bunches identified by the Mass Spectrometry of the bio-oil. Bio-oil that identified by GCMS obtained at a temperature of 500 °C and a biomass mass of 491 grams.

Table 8. showed that the primary pyrolysis identified products contains many aromatics and oxygenated compounds such as carboxylic acids, ketones, and aldehydes. The highest percent area was heavy hydrocarbon at the percentage of 39.51%, and 20.03% of the total area was acids. The presence of these aromatic and oxygenated compounds was related to its biopolymer textures such as cellulose, hemicellulose, and lignin (Branca *et.al.*, 2016).

Table 8. Chemical Compounds of Bio-oil from Empty Palm Oil Bunches according to the GC-MS Analysis

Peak	Name	Area (%)
1	Cyclobutylsilane	6.73
2	3,4,4-D3-3-Hydroxy-Cyclopentene	30.81
3	Pentane, 2-cycloropyl	27
4	Cyclohexane	0.56
5	Octadecanoid acid, Propanediyl ester	0.87
6	9-Octadecenoic acid	0.15
7	Hexadecanoic acid	0.17
8	11-Octadecenoic acid, Methyl ester	0.15
9	Ethenyl ester	0.16
10	(Hydroxymethyl)ethyl ester	0.42
11	Pentadec-7-ene, 7-bromomethyl	0.35
12	Propanediyl ester	16.05
13	Oleic acid, 3-hydroxypropyl ester	0.31
14	Bicyclo[10.1.0]tridec-1-ene	1.52
15	di-(9-octadecenoyl)-glycerol	12.89
16	Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester	0.84
17	4-hexenoic acid, 2-acetyl-2,4,5-trimethyl-, ethyl ester	0.17
18	Pyrimidine, 5-ethoxy-2-methyl-4-(methion)-	0.17
19	1,5,9-cyclododecanetriol	0.43
20	Muscone	0.28

Non-catalytic pyrolysis of biomass produces bio-oil with complex mixture of chemical compound. The results of this study are in accordance with previous reports where the thermal cracking of OPEFB produces gas and condensable product (bio-oil). The bio-oil obtained from this process consists of great range of phenols, alcohols, ketones, acids, and aldehydes, as well as small amounts of alkenes (Sembiring *et.al.*, 2015).

As lignocellulosic biomass, empty palm oil bunches contained cellulose, hemicellulose, and lignin. The cellulose content of empty palm oil bunches is 37.3% – 46.5%, while hemicellulose and lignin content are 25.3% – 33.8% and 27.6% – 32.5 %, respectively (Sudiyani *et.al.*, 2013). Cause high cellulose content, OPEFBs are potential to be transformed for the production of bio-oil, a worthy alternative for fuel by following ASTM D7544 standard.

CONCLUSION

Bio-oil is a condensed-liquid mixture that results from the thermal derivation of biomass containing hemicellulose, lignin, and cellulose as combustion fuels in engines and resources in chemical industries. The review of experiments showed that slow pyrolysis influenced by parameters such as temperature, mass, and feedstock. Optimal conditions affect the standards of quality for bio-oil. The experiments organized in this study using a response surface methodology to obtain the optimal conditions for the production of bio-oil from empty palm oil bunches. The optimal conditions of the variables as follows: Reactor temperature of 570.71ºC, the mass of empty palm oil bunches 420.71 gr. Based on the optimum condition, the predicted yield bio-oil content was 5.58%. This optimized condition was evaluated with the actual bio-oil yield in 5.6%. The chemical composition of bio-oil acquired was analyzed using GC-MS. These results showed that bio-oil obtained, which indicates the presence of the percentage of high cellulose content in empty palm fruit bunches, can be directly used as fuel oil.

ACKNOWLEDGEMENT

This research was supported by the RPI research scheme of UNDIP. The author would thank Chemical Engineering Department UNDIP for providing the facilities.

REFERENCES

Abdullah, N., Sulaiman, F, and Gerhauser, H, (2011), Characterisation of Oil Palm Empty Fruit Bunches for Fuel Application, *Journal of Physical Science*, 22(1), pp. 1-24.

Amin, N. A. S., and Akhtar, J., (2011), A Review on Process Conditions for Optimum Bio-oil Yield in Hydrothermal Liquefaction of Biomass. *Renewable and Sustainable Energy Reviews*, 15, pp. 1615-1624.

Azizi, K., Moraveji, M. K., Najafabadi, H. A., (2017), Characteristics and kinetics study of simultaneous pyrolysis of microalgae Chlorella Vulgaris, wood and polypropylene through TGA, *Biosource Technology*, 243, pp. 481-491.

Biswas, B., Pandey, N., Bisht, Y., Singh, R., Kumar, J., Bhaskar, T. (2017), Pyrolysis of agri-cultural biomass residues: a comparative study of corn cob, wheat straw, rice straw and rice husk, *Bioresources Technology*, 237, pp. 57–63.

Biswas, B., Singh, R., Kumar, J., Singh, R., Gupta, P., Krishna, B. B., & Bhaskar, T. (2018). Pyrolysis behavior of rice straw under carbon dioxide for production of bio-oil. *Renewable energy*, 129, pp. 686-694.

Branca, C., Di Blasi, C., & Galgano, A. (2016). Chemical characterization of volatile products of biomass pyrolysis under significant reaction-induced overheating. *Journal of analytical and applied pyrolysis*, 119, pp. 8-17.

Chan, Y. H., Dang, K. V., Yusup, S., Lim, M. T., Zain, A. M., & Uemura, Y. (2014). Studies on catalytic pyrolysis of empty fruit bunch (OPEFB) using Taguchi's L9 Orthogonal Array. *Journal of the Energy Institute*, 87(3), pp. 227-234.

Chiaramonti, D., Prussi, M., Buffi, M., Rizzo, A. M., & Pari, L. (2017). Review and experimental study on pyrolysis and hydrothermal liquefaction of microalgae for biofuel production. *Applied Energy*, 185, pp. 963-972.

Gashaw, A., Getachew, T. and Teshita, A, (2015), A Review on Biodiesel Production as Alternative Fuel, *Journal of Forest Products & Industries*, 4(2), pp. 80-85.

Guedes, R. E., Luna, A. S., & Torres, A. R. (2018). Operating parameters for bio-oil production in biomass pyrolysis: a review. *Journal of analytical and applied pyrolysis*, 129, pp. 134-149.

Crocker, M. (Ed.). (2010). *Thermochemical conversion of biomass to liquid fuels and chemicals*. Royal Society of Chemistry.

Ezekannagha, C. B., Ude, C. N., & Onukwuli, O. D. (2017). Optimization of the methanolysis of lard oil in the production of biodiesel with response surface methodology. *Egyptian Journal of Petroleum*, 26(4), pp. 1001-1011.

Chang, S. H. (2014). An overview of empty fruit bunch from oil palm as feedstock for bio-oil production. *Biomass and Bioenergy*, 62, pp. 174-181.

Loh, S. K. (2017). The potential of the Malaysian oil palm biomass as a renewable energy source. *Energy conversion and management*, 141, pp. 285-298.

Neto, C. J. D., Letti, L. A. J., Karp, S. G., Vítola, F. M. D., & Soccol, C. R. (2019). Production of biofuels from algae biomass by fast pyrolysis. In *Biofuels from Algae*, Chapter 18, pp. 461-473.

Sembiring, K. C., Rinaldi, N., & Simanungkalit, S. P. (2015). Bio-oil from fast pyrolysis of empty fruit bunch at various temperatures. *Energy procedia*, 65, pp. 162-169.

Shah, Z., Cataluña Veses, R., & Silva, R. D. (2016). Using GC-MS to analyze bio-oil produced from pyrolysis of agricultural wastes: discarded soybean frying oil, coffee and eucalyptus sawdust in the presence of 5% hydrogen and argon. *Journal of Analytical & Bioanalytical Techniques. Los Angeles*, 7(2), pp. 300-1-300-7.

Sudiyani, Y., Styarini, D., Triwahyuni, E., Sembiring, K. C., Aristiawan, Y., Abimanyu, H., & Han, M. H. (2013). Utilization of biomass waste empty fruit bunch fiber of palm oil for bioethanol production using the pilot-scale unit. *Energy Procedia*, *32*, pp. 31-38.

Thangalazhy-Gopakumar, S., Lee, C. W., Gan, S., Ng, H. K., & Lee, L. Y. (2018). Comparison of Bio-Oil Properties from Non-Catalytic and In-Situ Catalytic Fast Pyrolysis of Palm Empty Fruit Bunch. *Materials Today: Proceedings*, *5*(11), pp. 23456-23465.

Wang, D., Xiao, R., Zhang, H., & He, G. (2010). Comparison of catalytic pyrolysis of biomass with MCM-41 and CaO catalysts by using TGA–FTIR analysis. *Journal of Analytical and Applied Pyrolysis*, 89(2), pp. 171-177.