

## Optimization of Bio-Oil Pyrolysis Product from Palm Empty Fruit Bunches over H-Zeolite Catalyst using Response Surface Methodology (RSM)

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### Abstract

Bio-oil pyrolysis product considered as a promising resource of hydrocarbon compound that can be used as alternative fuel or other application. Palm empty fruit bunch (PEFB) based bio-oil converted into hydrocarbon through pyrolysis over sulfate activation natural zeolite. Here, we reported an optimization process of bio-oil pyrolysis specifically on temperature and catalyst dose variables by using response surface methodology (RSM). Prior conversion process, PEFB was analyzed to determine cellulose, hemicellulose and lignin content. Sulfate activation natural zeolite confirmed its acidity by ammonia and pyridine adsorption calculated by gravimetric method. Two independent variables namely temperature and catalyst weight used in optimization process by RSM whereas response variable is conversion percentage. Analysis result on cellulose, hemicellulose and lignin content are 45.39%, 30.36% and 20.5% respectively. Catalyst acidity determination based on ammonia and pyridine adsorption gave 1.002 mmol/g and 0.1994 mmol/g. Optimum condition of hydrocracking achieved at 568 °C and 2.1088 g catalyst weight with the product obtained at 62.21% conversion. The best product density is 1.086 g/mL obtained at hydrocracking temperature 554 °C and 2.0362 g catalyst. Based on GC-MS analysis, it was confirmed that the product comprises more straight-chain hydrocarbon than cyclic one. RSM calculation able to formulate the feasible model equation to predict the conversion percentage. The equation is; percent conversion = 60.059 + 14.268T + 9.783W - 25.649T<sup>2</sup> - 18.809W<sup>2</sup> + 3.114TW, whereas model equation for response variable on product density;  $\rho = 1.09103 - 0.12356T - 0.09744W + 0.11489T^2 + 0.28888W^2 - 0.00740TW$

**Keywords:** Bio-oil, Hydrocracking, Catalyst, Zeolite, Response Surface Methodology (RSM)

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### INTRODUCTION

Industries and most of transportation vehicles have used fossil fuel i.e. crude oil massively. Oil reserve on contrary depleted in a rapid rate (10% per-year) leaving countries with low oil production such Indonesia practically as net importer. The imbalance between supply and demand of crude oil triggered the effort of searching an alternative and sustainable energy. Several authors have studied biomass as raw material with a high potential to become alternative energy through variation conversion process [1,2]. Recently,

bio-oil gain more attention due to its abundance resources and carbon neutrality. Bio-oil derived from fast pyrolysis of carbonaceous materials such as waste biomass both from animal or plant remain. Various biomass has been reported in generating bio-oil such as sawdust, rice husk, chicken manure, oil palm empty fruit bunch and oil palm frond [3]. Indonesia produces approximately 40 billion ton per-year carbonaceous waste material generated from plantation across the country.

The Indonesia's position as the largest CPO producer in the world imply large palm plantation and result in enormous solid waste of biomass. Palm oil empty fruit bunch contains cellulose usually as the largest component (40-50%) and hemicellulose and lignin at smaller proportion [4]. These wastes traditionally used as boiler feeder or just buried as compost. The conversion of biomass into bio-oil carried out via fast pyrolysis with or without catalyst presence [5]. Fast pyrolysis by using metal catalyst resulted in an upgraded version of bio-oil that comprise of less aromatic and phenolic compounds. Bio-oil utilization for alternative fuel still facing many obstacles, mainly due to nitrogenous and oxygenated compounds make it a low quality of fuel [1].

Bio-oil must be processed further before used as alternative energy or fuel. Hydrocracking reported able to upgrade bio-oil into valuable hydrocarbon suited for fuel purpose among other techniques [6,7]. The process involves breaking up C-bond by thermal assistance supported by proper catalyst specifically designed for this purpose to obtain maximum hydrogenation as well as de-oxygenation [7]. Several compounds within bio-oil that need to be converted are acids, aldehydes, ketones, esters ethers and other. In a typical process of hydrocracking, these compounds were de-oxygenated and turn into hydrocarbon with various length of chain and branches [8]. Catalyst plays important role in a hydrocracking process. Noble metals as well as aluminosilicate minerals such as zeolite has been reported in catalytic hydrocracking [8–10]. Zeolite is widely used for this purpose because of its abundance and acid property that suited hydrocracking requirement [11]. Zeolite is crystalline mineral of aluminosilicate possessing pore uniformly distributed throughout on its surface. This material has been used for various application such as selective adsorbent, solid acid-base catalyst and support material for noble metal catalyst [12,13].

Natural zeolite undoubtedly can be used in converting bio-oil generated from waste biomass into valuable hydrocarbon. The economically combined material in processing bio-oil i.e. waste biomass and natural zeolite offered a break through effort in preserving natural resources and creating and alternative and sustainable energy. The complex composition of bio-oil nevertheless needs proper approach to obtain optimum condition of its conversion process [14]. Here, we reported optimization process condition of bio-oil hydrocracking over sulfate activation zeolite. Optimization carried out by using response surface methodology (RSM). Process optimization using RSM

employed both mathematics and statistic to obtain optimum value of response variable based on predetermined independent variables. To our best knowledge, no publication available regarding optimization of hydrocracking of bio-oil over sulfate activation natural zeolite.

## MATERIALS AND METHODS

### Materials

Natural zeolite used in this study purchased from Lampung. Natural zeolite was ground to obtain 200 mesh prior activation. Palm oil empty fruit bunches collected from local palm oil plantation. The biomass sample sorted, cleaned and pulverized before converted into bio-oil. Chemicals used in this study was purchased from Sigma-Aldrich high-grade quality as received.

### Methods

#### Preparation of sample and catalyst

The constituent of PEFB analyzed through Chesson-Datta method to evaluate cellulose, hemicellulose and lignin. The method used several solvents to dissolve particular substance whilst the residual was weighted. The relative percentage of cellulose, hemicellulose and lignin calculated at the end of procedure. Natural zeolite was activated using sulfate acid 1N. The solid catalyst soaked in the solvent for 6 hours; afterward the solid washed and dried in the oven at 110 °C. Activated natural zeolite acidity determined by ammonia and pyridine adsorption. This gravimetric method resulted in mmol of base adsorbed per-gram catalyst.

#### Hydrocracking of bio-oil

Bio-oil made by pyrolysis process in a batch reactor. This work carried out according to previous study [15]. The bio-oil product further processed in a hydrocracking reactor at various temperature (450 – 650 °C) and catalyst dose (1–3 g). Hydrogen gas streamed, which also served as carrier gas for the bio-oil sample at 1 L/min flow rate. Liquid product leaved the reactor was collected in a bottle. Hydrocracking process terminated once no more liquid come out from the reactor. The resulting liquid product weighted and ready for further analysis.

#### Liquid product analysis

The hydrocracking product determination performed by gas chromatography mass spectrometry. Solvent used for this purpose was n-hexane and the procedure conducted according to optimum setup of instrument toward hydrocarbon sample.

### Optimization of hydrocracking process

Optimization performed by response surface methodology using MatLab R2015a and Minitab16 software. The independent variables chosen were temperature (X1) and catalyst weight (X2) against response variable conversion percentage.

## RESULTS AND DISCUSSION

### Analysis result of PEFB

Palm oil empty fruit bunch consist of three major components namely: cellulose, hemicellulose and lignin. Cellulose is a polymer of  $\beta$ -D-glucopyranose bonded by  $\beta$ -(1,4) glycosidic bond with a high degree of polymerization and has no branch. Hemicellulose is a polymer of heterogeneous group of monosaccharides to forms xylans, xyloglucan, mannans and glucomannans, and others [16]. Analysis result shows the biomass sample has the composition as displayed on Table 1.

**Table 1.** Chemical composition of PEFB sample

No	Component	Amount (%)
1	Cellulose	45.39
2	Hemicellulose	30.36
3	Lignin	20.15

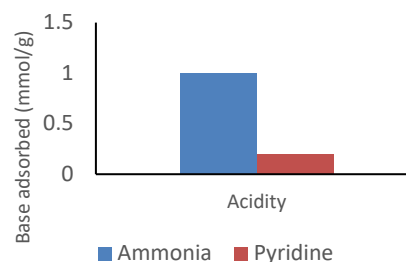
Biomass sample as stated earlier contains cellulose as major component compare to hemicellulose and lignin. Data shown on Table 1 confirms this fact, although it smaller than reported by another author, which obtained 55% cellulose [17]. As for hemicellulose, the sample contains 30.36% that is higher than reported by other author 15.32%. Both cellulose and hemicellulose undergo pyrolysis to form bio-oil particularly organic acids such as acetic acid and formic. Pyrolysis of hemicellulose contributes more to the formation of volatile component with less tar and chars. Lignin tend to form phenolic compound and required higher temperature on pyrolysis due to complex structure [18]. The presence of phenolic compound in bio-oil make this liquid product not suited for fuel application because it is highly corrosive [5].

### Acidity determination result

One of important properties a hydrocracking catalyst must has is acidity. Zeolite activated using sulfate acid and its acidity was calculated toward ammonia and pyridine adsorption by gravimetric method. The calculation result is shown on Figure 1.

Adsorption of ammonia and pyridine used to evaluate acid site on the surface of solid material especially for catalyst application. This method although is not a standard procedure on determining

acid site but informed the presence of acid site in different approach. Ammonia has smaller molecule size compare to pyridine as well as base strength. Both probe molecules considered as total acidity i.e. Brönsted and Lewis. Pan et al. (2019) reported that zeolite has both Lewis and Brönsted acid in various proportion [19]. These acid sites make zeolite a naturally solid acid material suitable for reaction catalyst i.e. hydrocracking, esterification, isomerization and alkylation.



**Figure 1.** Acidity of activated natural zeolite based on ammonia and pyridine adsorption

### Coding of DOE towards Conversion Yield and Product Density

The hydrocracking process was conducted and coded in 13 different experiments. The largest conversion of bio-oil occurred at 550 °C and 2 g catalyst dose, which is 62.65% showing 1.045 g/mL density (The RSM study display in Table 2).

The optimum result achieved by optimization process using software Matlab R2015a. Data processing of central composite design (CCD) using the same software indicates the optimum hydrocracking condition for bio-oil conversion. CCD analysis result reveals the effect of independent variable against conversion percentage. The result shows highest conversion by 62.21% obtained at 568.13 °C and catalyst weight 2.1088 g. Table 2 confirms the tendency of conversion percentage increment along with density declines occurred at 450 – 550 °C. This finding result as the effect of temperature to the reaction rate, which according to Arrhenius equation the two variables shows linear correlation until it reaches optimum value. Similar result had been reported by other author regarding the effect of temperature.

**Table 2.** Conversion percentage of bio-oil against temperature and catalyst weight

No	Temperature (°C)		Catalyst weight (g)		Conversion (%)	Density (g/mL)
	Actual	Code	Actual	Code		
1	450	-1	1	-1	33.26	1.5605
2	450	-1	3	1	37.57	1.5261
3	650	1	1	-1	39.38	1.2060
4	650	1	3	1	53.92	1.1568
5	691.4	1,414	2	0	50.38	1.1453
6	408.6	-1.414	2	0	12.02	1.1276
7	550	0	3,4	1.414	49.53	1.1451
8	550	0	0,6	-1.414	26.55	1.4758
9	550	0	2	0	60.21	1.0883
10	550	0	2	0	59.65	1.0915
11	550	0	2	0	58.71	1.1162
12	550	0	2	0	62.65	1.0450
13	550	0	2	0	59.08	1.1140

The density of hydrocracking product decreased along with temperature possibly due to increase of effective collision of reactant to form product of simpler compound. Increased in collision probability might affect the number of adsorbed reactant molecule and lead to enlarge surface reaction. In a heterogeneous catalysis, surface reaction is a dominant event in bond breaking of large molecule to produce smaller one. Smaller molecules in petroleum chemistry can be indicated by smaller density of a hydrocarbon liquid.

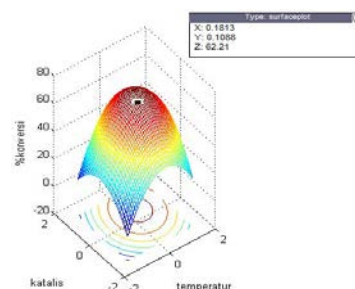
At higher hydrocracking temperature (550 – 650 °C), the conversion percentage tend to decrease whereas product density starts to increase. Zeolite-based catalyst used in this work has limit operational temperature, which caused the material to collapse and loose its activity. Catalytic hydrocracking cannot occur optimally once the catalyst decrease its functionality hence the conversion of bio-oil becomes low. High temperature also causes the adsorbed molecule on catalyst surface tend to desorbed and prevent from reacted with another reactant. Furthermore, in view of reactant molecule adsorption, high temperature decreases the collision probability on catalyst surface, which cause increases in product density in addition of low conversion percentage.

#### **Temperature and catalyst weight optimization towards conversion percentage**

Temperature and catalyst weight were setup as independent variable to evaluate its effect on the response variable i.e. conversion percentage designed base on response surface methodology. The calculation

for optimum condition determination carried out by using MatLab R2015a. The central composite design employed gave the effect of independent variable to the conversion of bio-oil. Percent of conversion by 62.21% obtained at 568.13 °C using catalyst as much as 2.1088 g.

The conversion of bio-oil increases along with higher temperature setup (450–550°C). Hydrocracking reaction prefer high temperature in order to break down larger molecules into smaller one. As the temperature increased, thermal energy transferred to C – C bond trigger it to break up followed by catalytic hydrogenation [19]. At higher temperature i.e. 550 – 650 °C, zeolite tends to suffer gradual structural break down that make the material less effective as hydrocracking catalyst. This situation lowers the conversion of bio-oil into hydrocarbon as depicted by Figure 2 [20].



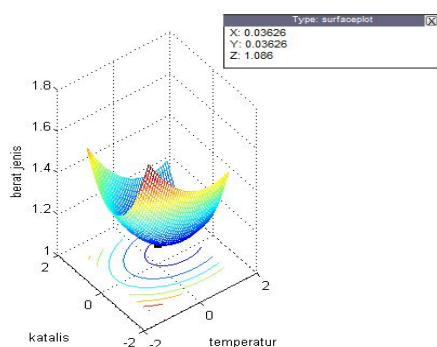
**Figure 2.** 3D response surface plots of the effect of temperature and catalyst weight against conversion percentage



### Temperature and catalyst weight optimization towards product density

Density defined as mass of material in a unit volume usually has the dimension of gram per mL. This parameter used in early development of petroleum industry to evaluate petroleum quality [21]. According to study reported by Porter & Lipson (2005), there is a correlation between liquid density and molecular chain of liquid hydrocarbon. Length of chain and thermodynamic of intramolecular interaction affect the liquid density [22]. Our data shows that as the hydrocracking temperature increased, molecular size of bio-oil becomes simpler and tends to have lower density. Chemical bond breaks down undoubtedly make the bio-oil molecules to form shorter chain of hydrocarbon.

The excess heat on higher temperature process however, might initiate further reaction such as coupling and result in a slight heavier molecule. The increased density above 550 °C is confirmed by the data obtained as depicted in Figure 3. In addition to coupling reaction, recombination of two radical species also contributes to larger molecule as hydrocracking product at higher temperature [23]. Analysis data by CCD method using MatLab software acquired optimum density of liquid product by 1.086 g/mL at 553.626 °C using catalyst weight 2.0362 g. Further calculation by using Minitab 16 to obtain support data for the optimization resulted optimization curve as displayed on Figure 3.



**Figure 3.** 3D response surface plots of the effect of temperature and catalyst weight against liquid product density

### Analysis result of conversion percentage and product density: stage 1

First run of experiment conducted according to factorial design 2k. Observation on the running procedures carried out 9 times whilst this first stage data process being input into Minitab 16 to determine model equation and analysis of variance. Mathematical

model of the optimization equation achieved from regression linear coefficient as follow:

$$\% \text{ conversion} = 50.4922 + 6.6175T + 5.7125W \quad (1)$$

$$\text{Density} = 1.2115 - 0.18095T - 0.0209 \quad (2)$$

The model equation informed that all variables gave positive response hence, the increase in temperature (T) or catalyst weight (W) will lead to conversion percentage increases. As for model equation for product density, it appears that all variables negatively responded toward both T and W variables. This finding imply that the product density will decrease as T and W decrease. The result obtained by using Minitab 16 software, still not represent the best model because the optimum point did not achieve hence the experiment went further into stage 2 by using CCD method.

### Analysis result of conversion percentage and product density: stage 2

Stage 2 experiment performed by using central composite design (CCD). In this stage, the data was processed to evaluate how the independent variables affects the response variable observed. The method designed so that it is possible to use independent variables simultaneously. The conversion data again treated by Minitab 16 to determine model equation and analysis of variance. The calculation result in form of model equation are as follow:

$$\% \text{ Conversion} = 60.059 + 14.268T + 9.783W - 25.649T^2 - 18.809W^2 + 3.114TW \quad (3)$$

$$\text{Density} = 1.091 - 0.123T - 0.097W + 0.114T^2 + 0.288W^2 - 0.007TW \quad (4)$$

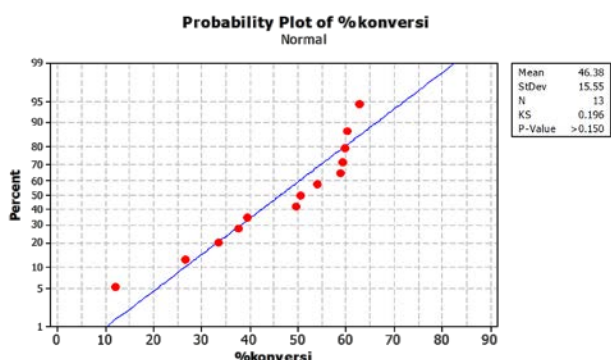
Model equation result indicate the conversion percentage gave positive response against T and W variables. This linear correlation implies the conversion percentage will increase as the T and W variables increase. The quadratic term however, suggest that when the T variable is doubled, it will cause conversion lower. As discussed earlier, zeolite cannot stand high temperature due to it will gradually suffer structural break down [20].

The model equation for response variable product density shows that negative response of T and W. This finding suggests smaller product density obtained when experiment uses low temperature and catalyst weight. In contrary, if the temperature and catalyst weight doubled, the product density will be substantial. During hydrocracking, proper temperature required to ensure reaction proceed in a more controllable condition. High temperature reaction tends to initiate a more complex mechanism which involve several reaction types simultaneously hence obtaining the

desired product is arduous. Thermal energy might be transferred massively to the reactant molecules and whilst it is result in smaller molecules, it also triggers coupling and recombination reaction, which form a larger molecule [23]. To evaluate whether or not correlation exist between independent variables and response variable, normality test was conducted accordingly.

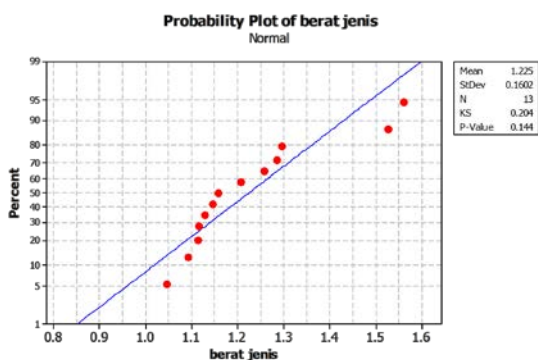
#### Normality test

Normality test performed to asses does the residual value produced normally distributed or not. The test was carried out using Kolmogorov-Sminov test.



**Figure 4.** Residual normality test of conversion percentage

The normality analysis conducted based on correlation plot of process yield against overall conversion percentage. If the statistical number of Kolmogorov-Sminov smaller than value from the table and p-value  $> 0.05$  then the residual value can be assumed normally distributed.



**Figure 5.** Residual normality test of product density

The statistical value of Kolmogorov-Sminov test ( $KS_{\text{calculated}}$ ) of the conversion percentage is 0.196 along with p-value 0.150, whereas the product density obtained 0.204 and p-value 0.144. The table value of Kolmogorov-Sminov test ( $KS_{\text{table}}$ ) at  $\alpha = 0.05$  is 0.206. Since the p-value above 0.05 and the value of  $KS_{\text{calculated}} < KS_{\text{table}}$ , then the residual value from model developed distributed normally. Result of the normality test

confirms that the independent variables T and W affects response variable (conversion and density) hence the mathematics model formulated is at the optimum value.

#### The product analysis of hydrocracking process using gas chromatography-mass spectrometry (GC-MS)

Data gathered from GC-MS shows that there is a decrease on the number of cyclic compounds along with increase on straight-chain hydrocarbon. This finding suggests there might be a break down process of cyclic to form a linear one [24]. The GC-MS analysis performed on hydrocracking liquid product with the substantial density (X1) i.e. hydrocracking at 450 °C, weight catalyst 1 g and liquid product with smallest density (X2) i.e. hydrocracking at 550 °C weight catalyst 2 g (X2). GC-MS result detected cyclic compounds in the liquid product of both highest (X1) and smallest density (X2).

Data recap on the Table 3 indicates cyclic compounds in X1 decreases its amount at Rf 7.75; 8.40 and 8.61 minute whereas X2 loses its cyclic compounds identify at Rf 7.75; 8.41 and 8.61. The number of decreases suggest that X1 contains more cyclic compound than X2 and the hydrocracking proceed optimal on X2. The reduced number of cyclic compounds along with increase of linear hydrocarbon concludes that break down of H-bond, glycosidic bond and finally cyclic ring occurred during hydrocracking process [25].

Linear hydrocarbon that increased its amount detected in X1 at Rf 19.65; 22.48 and 24.95 minute whilst X2 detected at Rf 19.68; 22.49 and 24.95 minute. Hydrocracking considered to be successful if the liquid product contains more linear hydrocarbon than cyclic. Catalyst used gave good performance to enhance reaction rate and assist the break down process of chemical bond within bio-oil.

Bio-oil used as feeder in this work contains chemical compounds of cellulose-derived, hemicellulose-derived as well as lignin-derived. Some authors identified compounds such as phenolic compound, levoglucosan as well as simpler hydrocarbon within bio-oil [24]. Table 2 shows the furan and phenolic compounds, which could be originated from further breaks down of cellulose and lignin-derived compounds. The complex mixture of bio-oil still far from complete conversion regardless how well-designed the treatment process. Optimization effort at least gave theoretical evidence on how the conversion of bio-oil should be conducted.

**Table 3.** Some cyclic compound identified by GC-MS in the hydrocracking product

Rf (X1)	Area X1 (%)	Rf (X2)	Area X2 (%)	Chemical formula	Chemical structure
7.75	0.66	7.75	0.39	C <sub>7</sub> H <sub>8</sub> O	
8.40	0.56	8.41	0.24	C <sub>8</sub> H <sub>10</sub> O	
8.61	0.55	8.61	0.15	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	

## CONCLUSION

The optimum hydrocracking condition of bio-oil from PEFEB was achieved at 554 – 568 °C using catalyst weight 2 g and conversion percentage 62.21% having product density 1.086 g/mL. Mathematical model developed according to RSM can be formulated as: conversion percentage = 60.059 + 14.268T + 9.783W – 25.649T<sup>2</sup> – 18.809W<sup>2</sup> + 3.114TW whilst for catalyst weight = 1.09103 – 0.12356T – 0.09744W + 0.11489T<sup>2</sup> + 0.28888W<sup>2</sup> – 0.00740TW.

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