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Used Lubricant Oil Pyrolysis Utilizing Microwave Irradiation and Lignite-Activated Carbon as Absorbent

Optimization with Formula Prediction of Kerosene Fraction

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Abstract:- About 50% of used lubricant oil turned out to be hazardous waste that can adversely impact health and the environment. One method for processing this waste is by cracking the hydrocarbon chain into liquid fuel fractions such as kerosene which can be done using a microwave-assisted pyrolysis process and activated carbon as a microwave absorber. The research have developed to optimize the temperature, microwave power, and material ratio variables of used lubricant oil pyrolysis process that assisted by microwave and absorbent from lignite to produce a high kerosene fraction. The pyrolysis process was carried out by mixing used lubricant oil and lignite absorbent, then pyrolyzing for 3 hours. The experimental design was made with the Box-Behnken model where the temperature level was set at 400 °C, 450 °C, and 500 °C, the power level was set at 400 Watt, 600 Watt, and 800 Watt, and the ratio level at 1:1, 1:1.3, 1:1.5 (w/w). The characteristics of the product obtained were tested by measuring the density parameter (15 °C) while the kerosene fraction was calculated by plotting the density data on the density curve versus the kerosene fraction. The optimization results obtained by data processing using the design expert application were the temperature of 400 °C, the power of 734,394 Watts, the ratio of 1,306 w/w with desirability value of 0.848 so that the prediction result for the kerosene fraction obtained was 97.503%.

Keywords:- *Kerosene; Lignite; Microwave; Pyrolysis; used Lubricant Oil.*

I. INTRODUCTION

Based on data processing from the Central Statistics Agency, the average increase of Indonesian motorbike users in 2016-2021 was 5.08% every year, so it could be estimated that the number of motorbike users will reach 132,548,381 units in 2023. This causes the rising oil demand as a lubricant for motorcycle engines, which is predicted to reach 1.4 GL by 2023 [1].

After being used for a certain period, the physical and chemical properties of lubricant oil will change due to high temperatures and pressure so that it no longer appropriate the requirements as a lubricant. As a result, used lubricant oil becomes waste because it is undesirable, toxic and hazardous material that can have negative impacts, both on human health and the environment [2].

Used lubricant oil consists (ULO) of 90% lube base oil and 10% additives. The basic compound of lubricant oil is thick oil that contains long-chain hydrocarbons (C_{31} to C_{40}). Because lubricant oil contains hydrocarbons which are the basic structure of liquid fuel, ULO has the potential to be reprocessed into liquid fuel containing fuel fractions such as kerosene with a hydrocarbon chain between C_{12} - C_{15}.

One method to process ULO is by cracking the carbon chain of that material through the pyrolysis technique that is assisted by microwave irradiation to produce liquid fuel fraction. Microwave irradiation has the advantages of more even and selective heating, meaning it depends on the dielectric properties of the material [3]. However, ULO has poor dielectric characteristics, so it cannot absorb microwave energy directly. To overcome this situation, it is necessary to add microwave-absorbing material. One material that can interact with microwaves is activated carbon that can be generated from various substances such as wood, coal, or agricultural wastes.

Some investigators have shown the success of ULO processing that serves fuel like diesel through pyrolysis treatment assisted by microwave. Mahari et al. converted waste shipping oil into diesel-like oil via microwave-assisted pyrolysis using activated carbon from coconut husk [4]. Meanwhile, Ramanathan and Santhoshkumar studied the utilization of commercial activated carbon as microwave absorbent on ULO pyrolysis assisted microwave and produced fuel like diesel [5]. In 2019, Santhoshkumar and Ramanathan tested the silicon carbide (SiC) capability as microwave absorbent to produce fuel like diesel from ULO that treated through assisted-microwave pyrolysis [6].

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In this research, the microwave-assisted pyrolysis was applied for treated ULO into kerosene and exploited activated carbon that was generated from lignite, as microwave absorbent. This study was conducted considering that kerosene has wide functions such as fuel for cooking to cleaning agents, jet fuel, heating oil or fuel for oil lamps. This fuel type can be used safely and efficiently to get great results in many areas. Because only a limited of oils can be used in such a wide range of applications and its low cost makes kerosene a very popular oil among many people [7]. Furthermore, the use of lignite as a basic material for absorbing microwaves in this research is intended to enrich the function of lignite. Lignite has weaknesses as a coal fuel but the amount of this material is quite potential especially in Indonesia [8].

The microwave-assisted pyrolysis would be worked out effectively if supported by compatible process variables, such as temperature (T), microwave power (P), and the ratio between activated carbon to ULO (R). In particular, this research aims to optimize those three process variables to obtain the high kerosene fraction.

II. METHOD

A. Preparation of Activated Carbon

Lignite as activated carbon raw material was obtained from coal mining in Samarinda City-Indonesia. Lignite-sized 12 mesh was immersed in 3 % $NH_4H_2PO_4$ and then in 20% $(NH_4)_2SO_4$ for 9 hours respectively. The ratio of lignite to each activator is 1g:1.25 mL. After chemical activation, the lignite was washed with H2SO4 and hot aquadest. The material then was heated at the temperature of 450°C for 30 minutes and continued at 950°C for 10 minutes in furnace so that producing lignite-activated carbon.

B. Experimental Design for Optimization

Optimization of pyrolysis process variables was carried out using the response surface method to exert the interaction of 3 independent variables, namely temperature (T), microwave power (P), and ratio (R). The variations of the independent variables were arranged as in Table I to collect data that will be used in the optimization process.

Table 1 Variations (Levels) of Independent Variable

Variables	**Level**		
	-1	**0**	**+1**
Independent Variables			
Temperature/T (°C)	400	450	500
Microwave Power/P (W)	400	600	800
Ratio/R (w/w)	1:1	1:1.3	1:1.5
Respon Variable	***Constraint***		
Kerosene Fraction/Y (%)	*Maximum*		

Based on the levels listed in Table 1, an experimental design was set up using the Box-Behnken method, so 16 condition formulas were obtained [9].

C. Pyrolysis Process

The ULO that were obtained from motorcycle garage was mixed with lignite-activated carbon in pyrolysis reactor flask. The reactor then was placed in a microwave oven that was equipped with temperature controller and connected with condenser series. Every condition that was formulated in Table II carried out and vapor product from pyrolysis was then passed through a series of condensers to get liquid product. The flow of nitrogen namely 200 mL/min was used to support flowing process of vapor to the condenser.

Table 2 Box-Benkhen Experimental Design Level

Formula	**Independent Variable Level**			**Kerosene Fraction**
	T	***P***	***R***	**Observation**
1	-1	-1	0	Y_1
2	-1	1	0	Y_2
3	1	-1	0	Y_3
4	1	1	0	Y_4
5	0	-1	-1	Y_5
6	0	-1	1	Y_6
7	0	1	-1	Y_7
8	0	1	1	Y_8
9	-1	0	-1	Y_9
10	1	0	-1	Y_{10}
11	-1	0	1	Y_{11}
12	1	0	1	Y_{12}
13	0	0	0	Y_{13}
14	0	0	0	Y_{14}
15	0	0	0	Y_{15}
16	0	0	0	Y_{16}

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D. Kerose Fraction Determination

Percentage of kerosene fraction was determined based on product density (ρ) measurement. Product density was analyzed with ASTM D-1298 procedure. The kerosene fraction (x) was then predicted using density-kerosene fraction formula that was generated from correlation of density versus kerosene fraction graph.

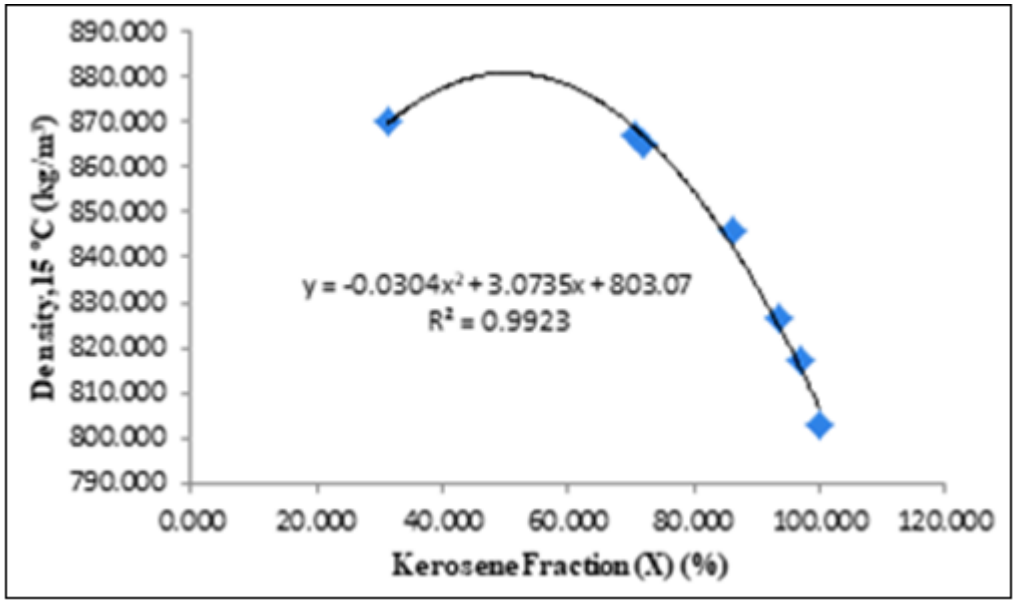

Fig 1 Correlation of Density Versus Kerosene Fraction

The correlation described in Fig. 1. was formulated using the basic data from previous research where the kerosene fraction of sample was measured using GC-FID instrument.

III. RESULTS AND DISCUSSION

➢ *The Results of Pyrolysis ULO based on the Experimental Design in Table II are Presented in the following Table:*

Table 3 Results of Density and Kerosene Fraction Analysis

Formula	$\rho_{,15\ °C}$ (kg/m^3)	Kerosene Fraction (%)
2	817.8225	96.0496
3	837.6046	88.2258
4	817.8624	96.0351
5	847.5557	83.5973
6	846.8763	83.9337
7	823.4374	93.9724
8	817.8225	96.0496
9	822.7580	94.2290
10	822.7580	94.2290
11	822.0986	94.4766
12	822.7580	94.2290
13	817.2030	96.2730
14	817.8624	96.0351
15	827.7136	92.3213
16	817.8624	96.0351

The ULO as raw material has a density of 15 °C, namely 871.6939 kg/m^3. After the pyrolysis process takes place, the value of the product density changes. Based on Table 3, the density value of the pyrolysis product has decreased to 81.8225-842.5602 kg/m^3. This indicates that a cracking process has occurred from ULO which has a long carbon chain into compounds with shorter carbon chains.

The data processing for optimization was solved using design expert -13 software. The analysis output is explained below

A. Fit Summary Model Analysis

The best model from the model selection test based on the sum of squares of the model sequence is the model that has a probability value of less than 5% (P < 5%).

Table 4 Fit Summary Model Analysis

Source	Sequential p-Value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0,0031	0,2192	0,5898	0,4244	
2FI	0,9785	0,1401	0,4641	-0,1834	
Quadratic	**0,0071**	**0,7812**	**0,8783**	**0,7259**	***Suggested***
Cubic	0,7812	0,2192	0,8225	-	*Aliased*

Based on Table 4, it can be seen that the model chosen to explain the effect of variable variations (temperature, power and ratio) on the response (kerosene fraction) is the quadratic model. Even though in the sequential p-value column the value is > 0.00001, which means the chance of model error is more than 5%, in the Lack of Fit column the p-value is 0.7812 > 0.1, which means the model mismatch does not affect the response. Then the difference between the adjusted R^2 and predicted R^2 values is 0.1524 < 0.2, which means the adjusted R^2 value is still within reasonable limits compared to predicted R^2. Therefore, the quadratic model was chosen because the R^2 value is closer to 1 compared to other models.

B. Anova Test

Anova is used to analyze data obtained by observing how much variation there is from an experiment with different levels of factors, usually two or more factors. The results of the anova test are presented in the following table.

Table 5 Kerosene Fraction Anova Test

Source	***Sum of Squares***	***df***	***Mean Square***	***F-value***	***p-value***	
Model	290.18	9	32.24	13.03	0.0027	*significant*
A-Temperature	0.4838	1	0.4838	0.1954	0.6739	
B-Microwave Power	203.55	1	203.55	82.24	0.0001	
C-Rasio	0.8852	1	0.8852	0.3576	0.5717	
AB	1.26	1	1.26	0.5085	0.5026	
AC	0.0153	1	0.0153	0.0062	0.9398	
BC	0.7576	1	0.7576	0.3061	0.6001	
A^2	1.72	1	1.72	0.6968	0.4358	
B^2	72.11	1	72.11	29.14	0.0017	
C^2	9.39	1	9.39	3.79	0.0994	
Residual	14.85	6	2.48			
Lack of Fit	4.02	3	1.34	0.3715	0.7812	*not significant*
Pure Error	10.83	3	3.61			
Cor Total	305.03	15				

In Table 5 the significant influence of a factor is indicated by the p-value which must be less than 0.05. The Anova test results show that temperature and the interaction between temperatures have an influence on the kerosene fraction produced, but not as much as the influence of other factors. The p-value for the temperature variable and its interaction is still greater than 0.05. This shows that the influence of temperature is not significant at the selected temperature interval. This is because the choice of temperature interval is at the temperature limit where microwave-assisted pyrolysis processes are usually carried out, namely in the middle-temperature range. The same thing can be seen also for the material ratio variable. However, the microwave power variable shows a significant influence because it has a p-value of 0.0001 and indicates that the power factor can significantly influence the recovery of the kerosene fraction at the selected level range. The Model F value of 13.03 implies that the model is significant. There is only a 0.27% chance that an F-value this large could be due to noise.

➢ *Equation (1) shows the model prediction for the kerosene fraction response, which is as follows:*

- Kerosene Fraction (%) = 95,17 +0,2459A + 5,04B + 0,3326C
- 0,5609AB – 0,0619AC + 0,4352BC
- + $0,6566A^2$ - $4,25B^2$ - $1,53C^2$ (1)

➢ *Where in :*

- A = Temperture/T (°C)
- B = Microwave Power/P (W)
- C = Ratio/R (w/w)

Based on the equation above, it shows that the response of the kerosene fraction is directly proportional to temperature, power and ratio. This can be seen from the constant values of the temperature, power and ratio variables which have a positive sign. The kerosene fraction will increase in proportion to increasing temperature, power and ratio. However, because the proposed model is quadratic, the yield of the kerosene fraction will decrease when it passes the optimum conditions. Fig. 2 illustrates the presence of

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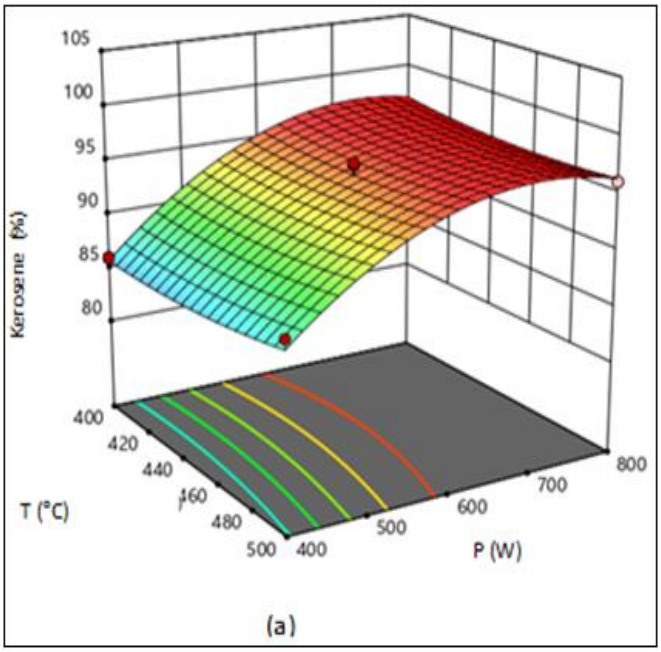
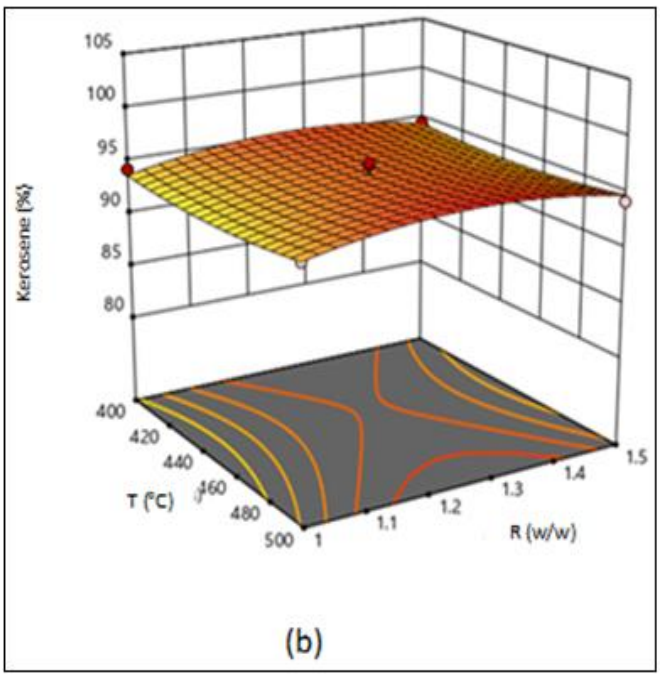
curvature as a peak condition even though the curvature contour obtained is not too steep. In the temperature-power relationship, shown in Fig.2 (a), the peak curvature contour is quite visible, as is the case in the power-ratio relationship, shown in Fig. 2 (c). Meanwhile, the contour of the peak curvature in the relationship between temperature and ratio does not look quite real as shown in Fig. 2 (b). The condition to be achieved is the maximum kerosene fraction, so that the influence of temperature, the influence of power, the influence of the ratio as well as interaction between power, ratio and temperature have an influence on maximizing the kerosene fraction, although not all of them have a significant impact.





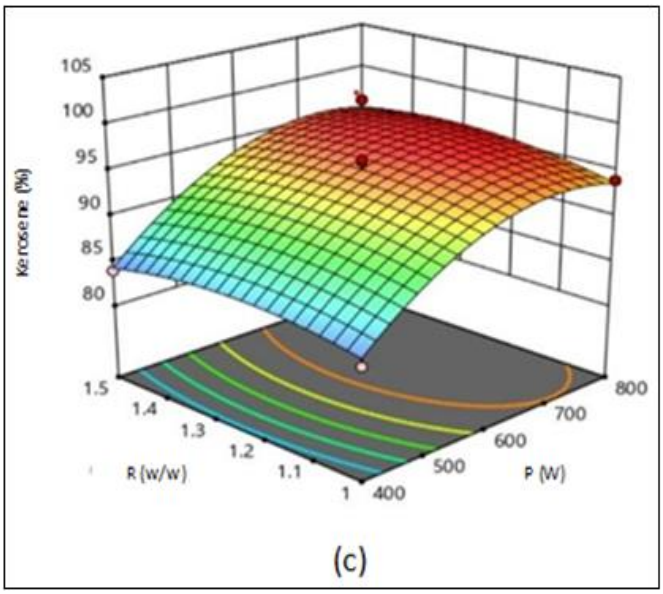


Fig 2 3D Model of Kerosene Fraction Response Test Results (a) Temperature vs Microwave Power, (b) Temperature vs Ratio, (c) Ratio vs Microwave Power

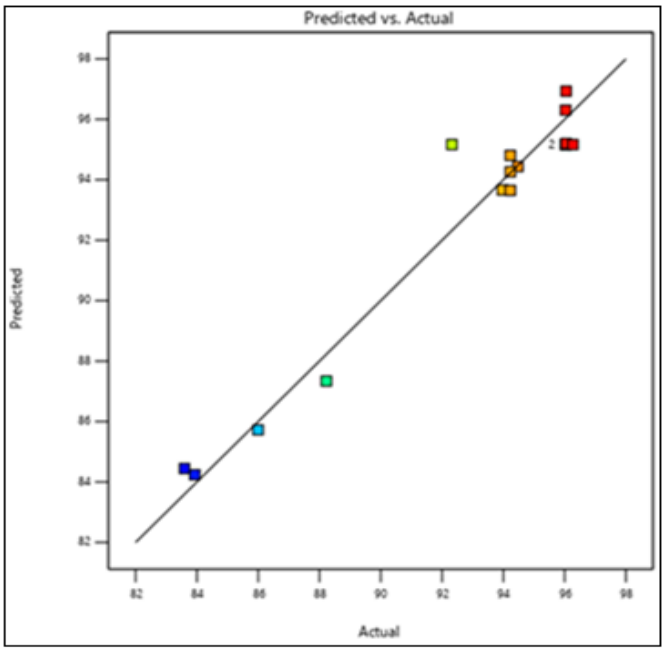


Fig 3 Plot Actual Kerosene Fraction Versus Prediction

The location of the actual kerosene fraction value is close to the predicted kerosene fraction value line with a coefficient of determination R^2 of 0.9513. From the coefficient of determination value, the correlation coefficient (R) value can be calculated which shows the strength of the relationship. The R value was obtained at 0.975, this value is considered very high or very strong. This can conclude that there is a good relationship between the actual and predicted values of the response and shows that the quadratic model chosen is adequate in predicting the response of the kerosene fraction.

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C. Optimization Results

Optimization is carried out to acquire the desired response. The aim of optimization is to obtain optimum conditions for the temperature, microwave power, and ratio variables and optimum results for the kerosene fraction response variable.

Table 6 Component Response of Optimization

Variable	Goal	Minimum Limit	Maximum Limit	Optimization Priority
T	is in range	400 ˚C	500 ˚C	5
P	is in range	400 Watt	800 Watt	3
R	is in range	1 (w/w)	1,5 (w/w)	3
Kerosene Fraction	maximize	83,5973%	100%	5

Kerosene fraction is a response variable which is the main target to get a high fraction with a value of 100%. Meanwhile, the variables temperature, microwave power, and material ratio are factor variables that will be optimized in order to obtain optimal values to gain a high kerosene fraction.

Table 7 Component Response of Optimization

No.	T (°C)	P (W)	R (w/w)	Kerosene Fraction (%)	Desirability	
1	**400.000**	**734.394**	**1.306**	**97.503**	**0.848**	***Selected***
2	400.000	734.536	1.308	97.503	0.848	
3	400.000	734.858	1.303	97.503	0.848	
4	400.001	733.973	1.310	97.503	0.848	
5	400.000	736.885	1.306	97.502	0.848	
6	400.000	736.141	1.314	97.501	0.848	
7	400.000	730.194	1.303	97.501	0.848	
8	400.001	733.429	1.316	97.501	0.848	
9	400.000	739.872	1.313	97.499	0.848	
10	400.001	735.165	1.319	97.499	0.848	
11	400.001	740.598	1.299	97.497	0.847	
12	400.001	727.362	1.313	97.496	0.847	
13	400.000	734.095	1.286	97.493	0.847	
14	400.000	743.831	1.299	97.491	0.847	
15	400.001	747.186	1.295	97.481	0.846	
16	400.000	747.153	1.326	97.478	0.846	
17	400.001	727.919	1.336	97.475	0.846	
18	500.000	707.296	1.292	97.293	0.835	
19	500.000	706.977	1.293	97.293	0.835	
20	500.000	707.978	1.296	97.293	0.835	
21	500.000	705.495	1.287	97.293	0.835	
22	500.000	704.743	1.293	97.293	0.835	
23	499.999	710.575	1.289	97.292	0.835	
24	500.000	709.868	1.299	97.291	0.835	
25	500.000	712.202	1.288	97.290	0.835	
26	500.000	718.171	1.314	97.270	0.834	
27	500.000	724.473	1.231	97.165	0.827	

Based on the optimization process that carried out with the design expert-13 software, 27 optimum formula solutions were produced which can be seen in Table 7. Process conditions with a temperature of 400 °C, microwave power of 734,394 Watt, and ratio 1,306 w/w are the optimal formula solution, because this process condition has the highest desirability value, namely 0.848 and is close to 1, thus providing the best optimization accuracy. Under these optimum conditions, a pyrolysis product will be produced that has characteristics close to the kerosene fraction optimization target, namely 97.503%.

IV. CONCLUTIONS

- *This Study has Established some Keys Information Related to Optimization Pyrolysis of ULO to Produce Kerosene with Assisted Microwave and Lignite-Activated Carbon, Namely:*

- The microwave power variable has a significant effect on the kerosene fraction obtained, while the temperature and material ratio variables show an insignificant effect in the range of values of the selected variables.

- Based on the optimization results using the response surface method and design expert-13 software processing, the solution given is a temperature of 400°C, microwave power of 734,394 Watts, and ratio of 1:1,306 w/w with predicted optimal kerosene fraction results of 97.503%.

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