Gas Production from Catalytic Cracking of Oily Sludge with Ni-Silica Catalyst

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Abstract

Oily Sludge (OS) derived from a Gas Process Plant underwent a catalytic cracking process, resulting Gas, CHP and Coke. Catalytic cracking is a chemical process that involves breaking down large molecules into smaller ones with the aid of a catalyst. The catalyst used in this process was Ni-Silica, with the Silica sourced from an Adsorbent. The optimization of the cracking conditions was achieved using Response Surface Methodology (RSM) with a Box-Behnken design. The optimized cracking conditions included varying temperature (713 K, 723 K and 733 K), time (50, 60 and 70 minutes) and the catalyst to OS ratio, which was 1:5, 1:6 and 1:7. Statistical analysis indicated that the relationship between the reaction condition variables and Gas production falls within the moderate category, with a coefficient of determination (R2) of 0.56. The calculated F-value also suggested that mathematical model generated is valid for the given range of conditions. The optimal reaction conditions were determined to be temperature of 725.29 K, time of 59.66 minutes and catalyst to OS ratio of 1:6.11, as derived from calculus analysis. Canonical analysis revealed that catalyst-to-sample ratio had the most significant influence on Gas production, followed by reaction time, while temperature had the least impact.

Keywords: *OS, Sillica, Ni-Metal, Catalytic Cracking, RSM*

1. Introduction

Oily Sludge (OS) is considered a potential source of energy due to its composition, which typically consists of 30% - 50% water, 30% - 80% oil, and 10% - 20% heavy metals. OS can be converted into fuel through a cracking process. [1]. Cracking is a process that involves breaking the C-C bonds of long-chain, high molecular weight hydrocarbons, resulting in hydrocarbons with shorter carbon chains and lower molecular weights. Cracking of OS can produce gas, the cracked product liquid (CPL), and coke. [2]. Cracking itself has two different conditions: thermal cracking and catalytic cracking. [3]. Thermal cracking is the thermal

decomposition of a material at atmospheric pressure [4]. Catalytic cracking is a cracking method that utilizes a catalyst. Catalytic cracking is a chemical degradation process aimed at achieving optimal results in terms of energy efficiency. The catalyst acts as a medium that can reduce the required reaction temperature and time [5]. Optimization of temperature, catalyst, and time is required in this research. One of the optimization methods is Response Surface Methodology (RSM), using a Box-Behnken design, which is commonly employed to find the optimal operating conditions for temperature, catalyst, and time [6][7][8]. Therefore, in this research, optimization is performed using RSM with a Box-Behnken design for catalytic cracking of OS feedstock using Ni-Silica catalyst. The variables considered, based on the literature review for comparison, include lower cracking temperatures of 713 K, 723 K, and 733 K, operation times of 50 minutes, 60 minutes, and 70 minutes, and catalyst to OS ratios of 1:5, 1:6, and 1:7.

2. Experiment

In this study, OS (Oily Sludge) is used as the feedstock, along with the Ni-Silica catalyst.

2.1. Materials

The materials used in this study, in addition to OS and Ni-Silica, include nitrogen gas, oxygen gas, hexane, solid Ni(NO3)2.9H2O, solid NaOH, and distilled water.

2.1.1. Preparation of OS

Before conducting the OS cracking, a filtration treatment is performed using a Buchner funnel assisted by a vacuum pump to separate the OS and water. The separated OS is then mixed with hexane at a 1:1 ratio, followed by stirring with a stirrer at room temperature for 3 hours. During this stirring process, it is expected that the oils present in the solid components of OS will be extracted. Afterward, a second filtration is carried out using the same method as described above, resulting in solid material with the OS.

The OS obtained from the second filtration is separated using a separating funnel for 15 minutes, resulting in two layers. The upper layer consists of OS, and the lower layer contains water. Subsequently, the OS in the upper layer undergoes vacuum distillation for 2 hours at a temperature of 342 K to separate hexane and OS. After this process, the OS is ready to be used as the feedstock for cracking.

2.1.2. Catalyst Preparation

The Ni-Silica catalyst is prepared through a hydrothermal process. The steps involved in the preparation are as follows: a 2% Ni-Nitrate solution (Ni(NO3)2.9H2O) is mixed with silica catalyst in an autoclave at a 1:10 ratio. The mixture is then placed in an oven at 423 K for 48 hours. Once the designated time is reached, the mixture is filtered. The filtered solid on filter paper is then placed in an oven for drying at 378 K for 12 hours.

3. Results and Discussion

In this study, OS is subjected to catalytic cracking using Ni-Silica, which results in gas, CHP, and coke. This discussion will primarily focus on the gas yield. The cracking results and the operating conditions used can be found in Table 1.

Tabel 1. Cracking Results

No	Reaction Conditions			Cracking Results (%)
	Temperature (Kelvin)	Time (minutes)	Catalyst to Oily Sludge Ratio	Gas Yield
1	713	50	1:6	18,50
2	713	70	1:6	28,38
3	733	50	1:6	17,58
4	733	70	1:6	26,88
5	713	60	1:5	14,63
6	713	60	1:7	23,38
7	733	60	1:5	16,21
8	733	60	1:7	38,71
9	723	50	1:5	54,58
10	723	50	1:7	31,38
11	723	70	1:5	58,17
12	723	70	1:7	19,38
13	723	60	1:6	20,34
14	723	60	1:6	10,63
15	723	60	1:6	13,42

In Table 1, you can see that temperature, time, and the catalyst to Oily Sludge ratio, with the Box-Behnken design, result in varying gas yields. This gas yield data will be used as Y and further analyzed using RSM. RSM is utilized to analyze the optimal conditions in this study. The gas conversion value is considered a dependent variable (Y), while the reaction conditions are treated as independent variables (X_1=temperature, X_2=time, and X_3=catalyst to Oily Sludge ratio). From this analysis, regression coefficients for gas can be incorporated into a second-order mathematical model as follows:

$$Yi = 14{,}79 + 1{,}81X_1 + 1{,}35X_2 - 3{,}84X_3 - 0{,}15X_1X_2 + 3{,}44X_1X_3 - 3{,}89X_2X_3 - 4{,}80{X_1}^2 + 12{,}84{X_2}^2 + 13{,}24{X_3}^2$$

The regression coefficients of the second order equation for the percentage of CHP yield can be observed in Figure 1.

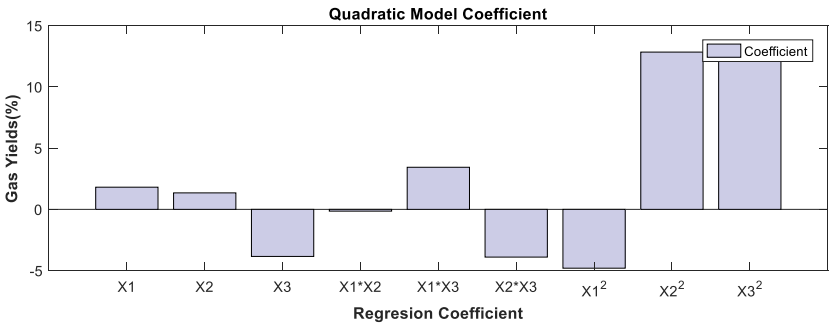

Figure 1. Graph of the Second-Order Equation Regression Coefficients against Gas Percentage

In Figure 1, the regression coefficients are in absolute values, and it's evident that the coefficient for X_3 is the highest among X_1 and X_2. Additionally, the coefficients for X_2*X_3 and X_3^2 also have relatively high values. This indicates that X_3 has a significant influence on the gas yield percentage.

Canonical analysis was also conducted to determine the sensitivity of the independent variables to the dependent variable, where the λ value is in absolute terms. The graphical representation of the canonical analysis can be observed in Figure 2.

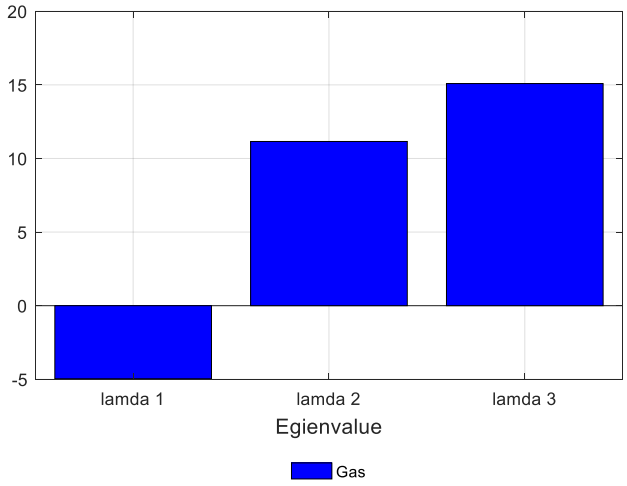

Figure 2. Graph λ_1, λ_2 and λ_3

For gas yield, λ1 = [-4.97], λ2 = [11.16], and λ3 = [15.09] were obtained, which indicates that the most sensitive response surface for gas is the catalyst to sample ratio, followed by reaction time, with temperature being the least sensitive.

Surface plots and contour plots illustrating the relationship between temperature and reaction time with gas yield percentage can be seen in Figure 3.

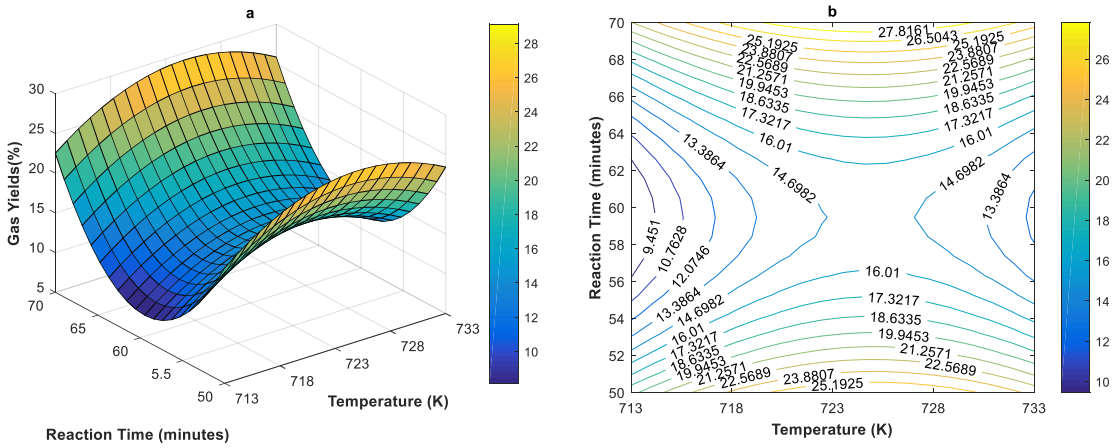

Figure 3. a) Surface Plot of Temperature and Time against Gas ; b) Contour Plot of Temperature and Time against Gas

In Figure 3, label a) shows that the graph of temperature and time against gas, obtained from catalytic cracking data, almost forms a minimum graph. To confirm this, it can be observed in the contour plot, where the purpose of the contour graph is to facilitate the interpretation of the surface plot and also to ascertain the type of the surface graph. Label b) demonstrates that the lines do not form circles, suggesting that this graph assumes a saddle shape. Surface plots and contour plots illustrating the relationship between temperature and the catalyst-to-sample ratio with gas yield percentage can be seen in Figure 4.

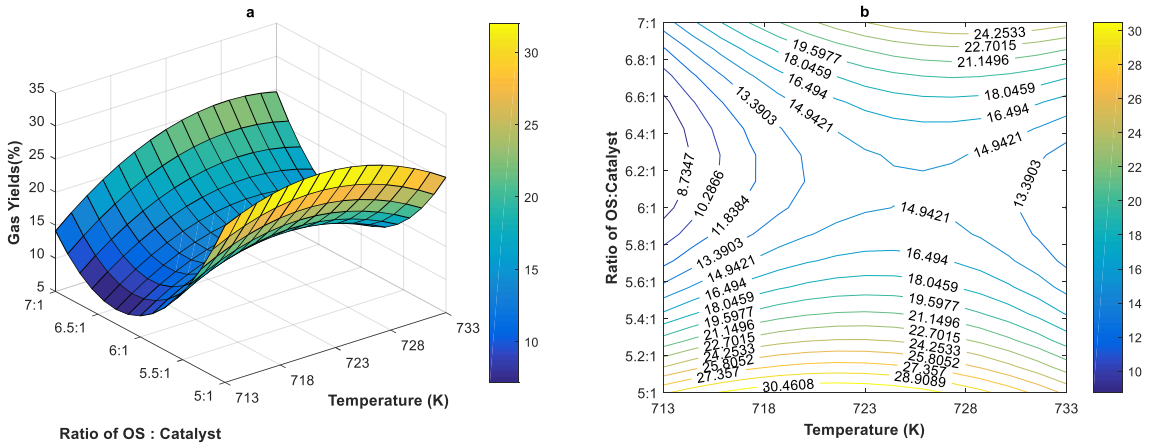

Figure 4. a) Surface Plot of Temperature and Catalyst to OS Ratio against Gas; b) Contour Plot of Temperature and Catalyst to OS Ratio against Gas

In Figure 4, label a) shows that the graph of temperature and the catalyst-to-OS ratio against gas, obtained from catalytic cracking data, assumes a saddle-shaped graph. This means that the optimal point between temperature and the catalyst-to-sample ratio is not a single point but rather scattered in a saddle-shaped region. Label b) represents a contour graph, where the purpose of the contour graph is to facilitate the interpretation of the surface plot and to confirm the type of the surface graph. In label b), it's evident that the lines formed do not create circles, indicating that this graph assumes a saddle shape. Surface plots and contour plots illustrating the relationship between reaction time and the sample to catalyst ratio with gas yield percentage can be seen in Figure 5.

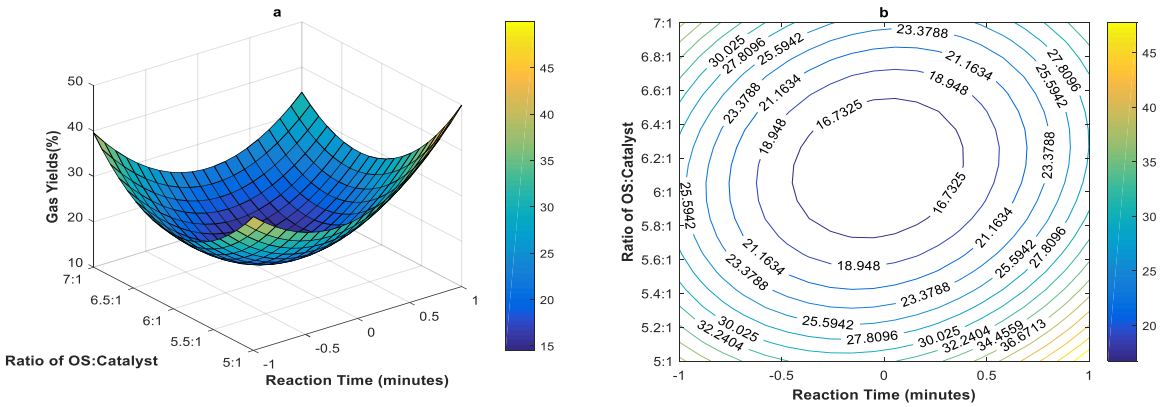

Figure 5. a) Surface Plot of Time and Catalyst to Sample Ratio against Gas; b) Contour Plot of Time and Catalyst to Sample Ratio against Gas

In Figure 5, it can be observed that the graph of reaction time and the sample-to-catalyst ratio against gas, obtained from catalytic cracking data, appears to take on the shape of a minimum graph. To provide further clarity, it can be compared with the contour plot in label b). In label b), the lines formed create circular patterns, indicating that this graph forms an optimal minimum.

Based on the explanation provided above, a comprehensive RSM analysis table can be constructed, which can be found in Table 2.

Table 2. Results of RSM Analysis on Cracking Data

Results (Y)	Statistical Parameters				The accepted model or rejected model	Canonical analysis			Sensitivity	Types of charts		
	R^2	F count	F Table (9,2)			λ_1	λ_2	λ_3		X_1X_2	X_1X_3	X_2X_3
		LF	$\alpha = 0,05$	$\alpha = 0,01$								
Gas	0,56	16,39	19,38	99,38	Accepted	-4,97	11,16	15,09	T<t<ks	*Saddle*	*Saddle*	Minimum

From Table 2, it can be seen that all the mathematical models obtained using RSM are acceptable based on their statistical parameters. Additionally, the sensitivity analysis for gas yield indicates that the most sensitive response surface for gas is the catalyst-to-OS ratio, followed by time, with temperature being the least sensitive factor. RSM analysis also provides the optimal reaction conditions for the catalytic cracking study with Ni-Silica catalyst, as shown in Table 3.

Table 3. Optimal Operating Conditions

No	Conversion for	Optimal variable values		
		Temperature (Kelvin)	Time (Minutes)	K/S
1	Gas	725,29	59,66	1:6,11

From Table 3, it can be observed that the optimal operating conditions obtained from the RSM analysis are as follows: a temperature of 725.29 K, a reaction time of 59.66 minutes, and a catalyst-to-OS ratio of 1:6.11. These conditions are predicted to yield a gas yield of 14.77%.

4. Conclusion

Catalytic cracking of OS using Ni-Silica catalyst has been demonstrated to yield gas. RSM with the Box-Behnken design is capable of providing an accurate mathematical equation to determine the optimal operating conditions, considering variations in temperature, time, and catalyst-to-OS ratio to determine the optimum gas yield. RSM analysis can also provide information about the sensitivity of the operating conditions. In this study, it is shown that the most sensitive response surface for gas yield is the catalyst to OS ratio, followed by time, with temperature being the least sensitive factor.

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