

Oxidative Desulfurization using Centrifugation-Reactor with Hydrogen Peroxide Oxidizer and Formic Acid Catalyst to Reduce Sulfur Content in “Dexlite” Fuel

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Abstract

Oxidative desulfurization (ODS) method can be used to reduce sulfur compounds in diesel fuel. ODS consists of two stages, namely oxidation of sulfur compounds and separation of sulfone as an oxidation product. The process occurs in two different equipment. The centrifugation-reactor is an equipment that combines reactor for the ODS with centrifuge for the sulfone separation process. This study aims to test centrifugation-reactor and obtain parameters for optimal operating conditions for the ODS. The oxidizer used is hydrogen peroxide, while the catalyst is formic acid. The variables tested were temperature, catalyst-fuel ratio, stirring speed, and residence time. Indonesia diesel “Dexlite”, before and after the ODS process was tested using FTIR to obtain the value of total sulfur content. The results of this study gave the best desulfurization percentage of 22.58% at temperature of 30 °C, catalyst-fuel ratio of 1:20, stirring speed of 300 rpm, and residence time for 5 minutes.

Keywords: Centrifugation-Reactor, Dexlite, Formic Acid, Hydrogen Peroxide, Oxidative Desulfurization.

1. Introduction

Petroleum products such as diesel fuel is an important product to meet energy needs in Indonesia. Based on the cetane number, diesel fuel produced commercially in Indonesia is classified into three types: “Biosolar”, “Dexlite”, and “Pertamina Dex”. The sulfur content in diesel fuel differs as well. “Biosolar” has a cetane number of 48 and the highest sulfur content (3,500 ppm) when compared to “Dexlite” and “Pertamina Dex”. “Dexlite” has a maximum sulfur content of 1,200 ppm and a minimum cetane number of 51. “Pertamina Dex” is a type of diesel fuel in Indonesia that has the highest cetane number, 53, and a maximum sulfur content of 300 ppm, which meets Euro III standards. However, the sulfur content of commercial diesel products in Indonesia is still relatively high when compared to the standards applied by other countries. The Euro VI standard limits a maximum sulfur content in diesel fuel to 10 ppm and the American emission standard, namely the EPA standard limits it to 15 ppm [1]. The sulfur content in diesel fuel must be reduced because it can cause environmental, health, and engine damage problems.

The method used to reduce the sulfur content in fuel is oxidative desulfurization (ODS). In the ODS process, the presence of an oxidizer causes sulfur compounds in the fuel to undergo oxidation to sulfones and sulfoxides [2]. Then the sulfone and sulfoxide compounds are separated from the mixture using adsorption or extraction methods. The ODS process has an advantage in being able to remove aromatic and cyclic sulfur such as thiophene, dibenzothiophene (DBT), benzothiophene (BT), and their derivatives that the hydrodesulfurization (HDS) approach are unable to. Sulfur's strong affinity for oxygen allows the selective attachment of oxygen to organic sulfur and thiophene derivatives without breaking the C-C and C-S bonds. Furthermore, the ODS process can run in mild conditions and does not require hydrogen which is expensive [3].

Factors affecting the ODS process are the type of oxidizer and catalyst. The oxidizing agent used in this research is H₂O₂. H₂O₂ is used because of its relatively low cost, environmental friendliness, and commercial availability. H₂O₂ also provides high selectivity for the oxidation of thiophene sulfur to sulfone [3]. The catalyst used is formic acid because it is easy to obtain, relatively inexpensive, and provides a good sulfur removal rate. The success of this combination of oxidizer and catalyst was reported by Joskić, Margeta, and Sertić-Bionda [4] who conducted ODS experiments on diesel fuel with H₂O₂ oxidizer, formic acid catalyst, and separation by adsorption method resulting in sulfur removal of 98%.

The most common method of separating sulfone as the result of oxidation process is solvent extraction. This causes the ODS process to not run continuously. Salsabila [5] has created equipment that combined a reactor with the CSTR type and centrifuge so that the ODS process can run continuously. The way this equipment works is that reactants, namely diesel fuel, oxidizing agent, and catalyst enter from the bottom of the equipment, namely the reactor and undergo an oxidation reaction. The oxidized liquid containing sulfone will rise to the extractive centrifugal section due to an increase in the fluid level in the reactor. The liquid will experience rotation and centrifugal force causing fluid separation based on density. Diesel fuel has a lower density than sulfone, oxidizer, and catalyst so diesel fuel will separate from those materials and comes out of the equipment. Research using the centrifugation-reactor for the ODS process has only been tested using Indonesia diesel “Biosolar” so this research will try to test the other type of diesel, namely “Dexlite”.

There are several differences between Biosolar and Dexlite. Biosolar is a diesel fuel with a mixture of biodiesel or vegetable oil with diesel fuel. Biosolar B30 means it has 30% vegetable oil content and 70% diesel fuel. The vegetable oil content is indicated by the fatty acid methyl ester (FAME) content in the fuel specifications. The FAME content makes Biodiesel more polar when compared to other diesel fuels which only contain pure diesel such as Dexlite. Apart from the difference in polarity, another difference between Biosolar and Dexlite is the cetane number and sulfur content, as previously mentioned.

Variables that will be varied in this study are temperature, catalyst-fuel ratio, residence time, and stirring speed (rpm). The purpose of this research is to get the centrifugation-reactor performance for different solar types. The difference in composition between Biosolar and Dexlite is the reason for carrying out variable variations to find out the optimal conditions for the ODS process. Variation of temperature is carried out because temperature can accelerate the rate of oxidation reactions and the ODS process is affected by temperature, variations in the catalyst-fuel ratio due to differences in sulfur content, variations in residence time because it affects the length of contact between reactants, and variations in stirring speed due to differences in polarity between Biosolar and Dexlite.

Testing for sulfur content before and after ODS process can be carried out using a fourier transform infrared (FTIR) instrument. This analysis uses research data and formulas that have been published by Az-Zahra et al. [6]. The research results of this study are meant to be used as a reference for the ODS method, which may be applied to enhance the quality of diesel fuel in Indonesia by lowering the sulfur contents.

2. Experimental Procedure

The materials used in the ODS process are diesel fuel, oxidizer, and catalyst. The type of fuel used in this study is a commercial fuel in Indonesia, namely Dexlite. In this study, 50%-w hydrogen peroxide was employed as an oxidizer. H_2O_2 is an extremely strong oxidizing agent, as indicated by its high reduction potential value of 1.78 V [7]. This value is higher when compared to several other oxidizing agents such as $KMnO_4$ of 1.67 V, $Fe_2(SO_4)_3$ of 1.30 V, and $NaOCl$ of 0.94 V. H_2O_2 also has a large amount of active oxygen content of 47.1% [7]. Formic acid is the most widely used catalyst in the ODS process when compared to other carboxylic acids [8]. In addition to its good ability to reduce sulfur content as has been proven by previous studies [5, 9], formic acid is also easy to obtain, relatively inexpensive, and has high selectivity so that in this study it will be used as a catalyst.

The equipment used in this study is a centrifugation-reactor. The centrifugation-reactor is an equipment that combines a reactor for the ODS process with a centrifuge to separate the sulfone content from fuel. The combination of the reactor and centrifuge allows the entire ODS process to run in just one device so that the process becomes continuous. A sketch of the centrifugation reactor used in this study can be seen in Figure 1.

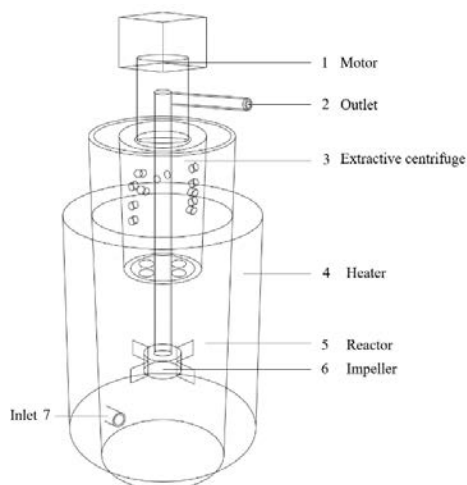


Fig. 1. Centrifugation-Reactor

The centrifugation-reactor consists of two parts where two different processes occur. At the bottom of the equipment is a reactor where the oxidation process stages occur. The reactants for the ODS process consist of diesel fuel, oxidizer, and catalyst. The oxidizer and catalyst are first introduced into the reactor. The quantity of oxidizers is fixed by a molar ratio of 89:1 (O:S), while the catalyst used is adjusted to the variable of catalyst-fuel ratio (v/v) employed, which are 1:5, 1:10, 1:15, and 1:20. After introducing the oxidizer and catalyst, the equipment is turned on by pressing the *Power On* button. Then, the heater and the stirring speed were turned on and adjusted to achieve the desired variable variation, specifically at temperatures of 30, 50, and 70 °C. The stirring speed in the first 12 samples was set at 300 rpm. After obtaining the best temperature and catalyst-fuel ratio, the stirring speed varied at 200, 300, 400, and 500 rpm. Following the set-up of the desired reactor operating conditions, diesel fuel is fed into the reactor through the inlet section continuously. The reactants then undergo an oxidation process so that the sulfur compounds in diesel fuel are converted to sulfones.

At the top of the equipment there is a centrifuge which is used for the separation of sulfone from diesel fuel. The liquid resulting from the oxidation, which is a mixture of diesel fuel and its sulfone content, will rise to the extractive centrifugal section. This is due to an increase in the fluid level in the reactor due to the diesel being fed continuously. In the extractive centrifugal section, the liquid will experience rotation due to the frictional force on the centrifugation wall. This rotation forms a vortex and centrifugal force will cause the separation of fluids based on their density. The fluid with a lower density will come out of the top of the equipment, while the fluid with a heavier density will fall back into the bottom of the equipment. Dextlite has a lower density than sulfone, which is a maximum of 860 kg/m³, while DBT-sulfone has a density of 1396 kg/m³. Then the diesel which has been reduced and has been separated from its oxidized sulfur content exits the equipment through the outlet at the top of the reactor. The diesel flows out and is accommodated in a beaker glass. The length of time required for the ODS process from the time diesel fuel is fed into the reactor until it exits through the reactor outlet is calculated as the residence time. The initial 16 samples used the residence time of 3 minutes, then after the other optimal variables were obtained, residence time were varied for 2, 3, 4, and 5 minutes.

3. Method of Analysis

Quantitative analysis using FTIR was carried out by comparing the content of the compound to be calculated against the unchanged compound. This quantitative analysis method was used by Az-Zahra et al. [6] in a previous study for calculating the sulfur content in Biodiesel fuel.

The wavelength used by Az-Zahra et al. [6] to identify the presence of sulfur content in Biodiesel is 1169 cm⁻¹. The reference wavelength used is 1458 cm⁻¹ which indicates an aromatic ring. Furthermore, the calculation of sulfur content can be done by making a calibration curve. The use of FTIR in the calculation of sulfur content has an accuracy of 62% against ASTM D-4294 which is an international standard test for measuring sulfur

content in petroleum products. Therefore, this study will use the equation published by Az-Zahra et al. [6] to calculate the sulfur content in Dexlite fuel before and after ODS process.

After the total sulfur content in the ODS sample (TSC_T) is obtained, the results are compared with untreated Dexlite (TSC_U) which has not undergone the ODS process so that the percent desulfurization value is obtained. Percent desulfurization can be calculated using the following equation:

$$\text{Desulfurization (\%)} = \frac{TSC_U - TSC_T}{TSC_U} \times 100\% \quad (1)$$

4. Results and Discussion

Table 1 shows the overall data for each sample as result of the data processing conducted. It could be seen that the ODS process reduced the total sulfur content of Dexlite from 266.78 ppm to a lesser amount. As indicated in Table 1, the four independent variables used in this study were temperature, catalyst-fuel ratio, stirring speed, and residence time.

Table 1. Result Summary of the Research

Sample Name	Operating Conditions				Sulfur Content (ppm)	Desulfurization (%)
	Temperature (°C)	Catalyst-Fuel Ratio (v/v)	Stirring Speed (rpm)	Residence Time (minutes)		
Untreated Dexlite	-	-	-	-	266.78	-
Blank Sample	30	-	300	3	257.81	3.36
Sample 1	30	1:10	300	3	225.33	15.54
Sample 2	50	1:10	300	3	225.42	15.50
Sample 3	70	1:10	300	3	240.19	9.97
Sample 4	30	1:5	300	3	227.10	14.88
Sample 5	50	1:5	300	3	229.02	14.15
Sample 6	70	1:5	300	3	240.36	9.90
Sample 7	30	1:15	300	3	221.58	16.94
Sample 8	50	1:15	300	3	223.01	16.41
Sample 9	70	1:15	300	3	227.27	14.81
Sample 10	30	1:20	300	3	209.27	21.56
Sample 11	50	1:20	300	3	222.78	16.49
Sample 12	70	1:20	300	3	225.19	15.59
Sample 13	30	1:20	200	3	221.48	16.98
Sample 14	30	1:20	300	3	209.27	21.56
Sample 15	30	1:20	400	3	210.74	21.01
Sample 16	30	1:20	500	3	212.85	20.22
Sample 17	30	1:20	300	2	219.63	17.68
Sample 18	30	1:20	300	3	209.27	21.56
Sample 19	30	1:20	300	4	207.84	22.10
Sample 20	30	1:20	300	5	206.55	22.58

4.1 ODS Test Results on Blank Sample

The blank test was carried out at operating conditions of 30 °C, stirring speed of 300 rpm, and residence time of 3 minutes with the amount of oxidizing agent using an O/S molar ratio of 89:1. Furthermore, the results of the blank test will be compared with the ODS sample under the same operating conditions but using a catalyst, namely Sample 4 with the addition of catalyst using a catalyst-fuel ratio of 1:5.

The blank ODS test without a catalyst yielded a decrease in sulfur content from 266.78 ppm to 257.81 ppm or a desulfurization percentage of 3.36%. On the other hand, the addition of a catalyst increased the desulfurization percentage to 14.88%. The results differences with and without the presence of this catalyst are quite significant. The presence of a catalyst in the ODS system can encourage the formation of reactive oxygen thereby accelerating the ODS process. In addition, the presence of a catalyst is also useful for bringing together the two reactants, namely hydrogen peroxide as oxidizer and Dexlite, which has a different polarity. However, these results show that the ODS process using a centrifugation-reactor can be carried out without a catalyst with a decrease in sulfur content which is worse than using catalyst, according to the research of Rajendran et al. [9]. Given the significance of a catalyst in the ODS process, the test for ODS in this study will use a formic acid as catalyst.

4.2 Effect of Temperature on Desulfurization Percentage

The temperature variations used are 30, 50, and 70 °C. For testing this variable, the stirring speed and residence time were set at 300 rpm for 3 minutes. The effect of temperature on the desulfurization is presented in graphical form which can be seen in Figure 2.

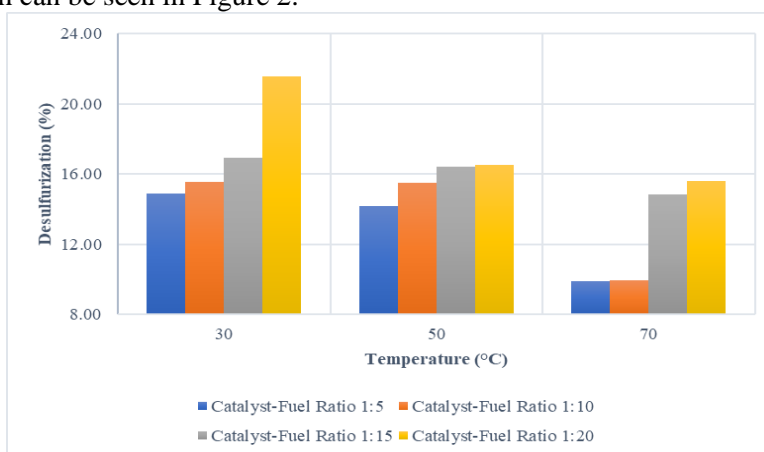


Fig. 2. Effect of Temperature on Desulfurization Percentage

Figure 2 shows that the increase in temperature causes a decrease in the percentage of desulfurization. This could be due to the oxidizing agent used, namely hydrogen peroxide, decomposing into water and oxygen at high temperatures. The decomposition of hydrogen peroxide is also evidenced by the presence of gas coming out of the reactor side during the sample running when the temperature is increased and starts to reach 40 °C. Every 10 °C increase of the temperature can increase the decomposition rate of hydrogen peroxide by 2.3 times [10]. This shows that at higher temperature, the more hydrogen peroxide is decomposed so that the amount of oxidizing agent used for ODS decreases.

The ODS process is better at low temperatures because the ODS reaction using hydrogen peroxide as an oxidizer and formic acid catalyst is an exothermic reaction. The exothermic reaction is better at low temperatures so that the next ODS process will use the lowest experimental temperature of 30 °C because it gives the highest desulfurization percentage of 21.56% at a catalyst/fuel ratio of 1:20.

4.3 Effect of Catalyst-Fuel Ratio on Desulfurization Percentage

Formic acid is the most common type of carboxylic acid used as a catalyst in ODS. The effect of using a catalyst is observed by comparing the amount of catalyst to fuel in volume/volume units. Increasing the catalyst/fuel ratio from 1:20, 1:15, 1:10, 1:5 lowered the average percentage of desulfurization from 17.88%;

16.05%; 13.67%; and to 12.98% sequentially. Figure 3 shows the effect of varying the catalyst-fuel ratio on desulfurization.

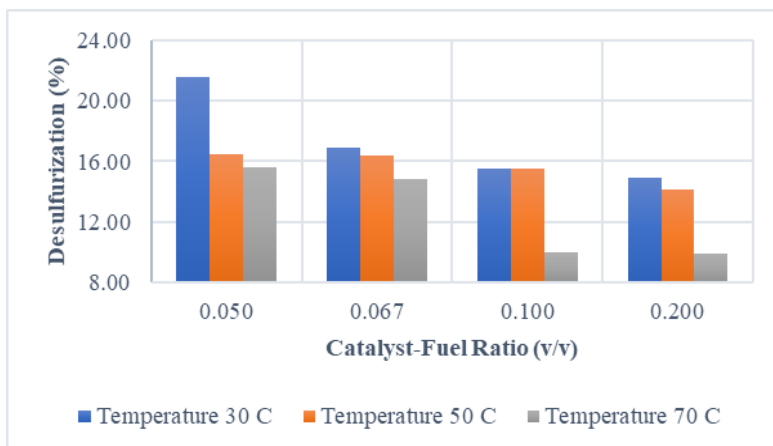


Fig. 3. Effect of Catalyst-Fuel Ratio on Desulfurization Percentage

An increase in the catalyst-fuel ratio causes a decrease in the percentage of desulfurization. This can occur because the greater amount of catalyst in the ODS system can lower the concentration of oxidizer and sulfur. The reaction is directly proportional to the concentration so that a decrease in the concentration of the oxidizing agent causes the conversion of the reaction, namely the conversion of sulfur to oxidized sulfur, to decrease as well.

The catalyst used is formic acid which is a polar compound. More catalyst results in more polar fractions in the reactor. Diesel fuel is a non-polar fraction and because the large amount of catalyst increases the polar fraction, the mixing that occurs is not good. Because of the poor mixing, the sulfur conversion rate may drop. Furthermore, the amount of catalyst at the minimum catalyst-fuel ratio of 1:20 may be adequate for the catalyst required in the ODS process, such that the addition of catalyst does not increase the percentage of desulfurization.

4.4 Effect of Stirring Speed on Desulfurization Percentage

After obtaining the best value of temperature and catalyst-fuel ratio, the stirring speed is tested. The stirring speed varied to 200, 300, 400, and 500 rpm with a constant variable temperature of 30 °C, a catalyst-fuel ratio of 1:20, and a residence time of 3 minutes. Figure 4 shows the ODS results for different stirring speeds.

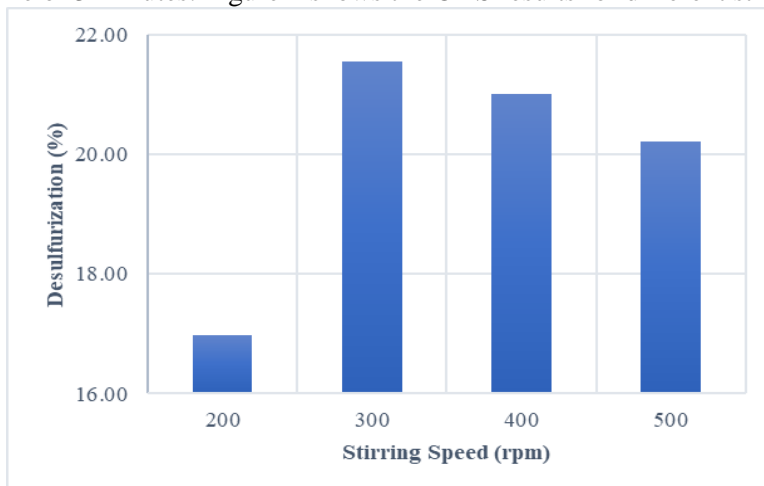


Fig. 4. Effect of Stirring Speed on Desulfurization Percentage

Desulfurization increased from 16.98% to 21.56% when the stirring speed was raised from 200 rpm to 300 rpm. The contact and mixing conditions between the two phases, which are the oxidizing agent and catalyst with

diesel fuel, affect the interface transfer and emulsion droplets. Because of the low stirring speed, the emulsion contains fewer droplets, resulting in a low reaction rate with a smaller contact surface area. Increasing the stirring speed results in more droplets of smaller size. The formation of smaller emulsion droplets expands the interfacial area accessible for the ODS reaction. This results in a high mass transfer rate and a faster reaction because the catalyst is well dispersed at the interface. This theory is in accordance with the results obtained from increasing the stirring speed from 200 rpm to 300 rpm which also increases the percentage of desulfurization.

Conversely, increasing the stirring speed from 300 rpm to 400 rpm and from 400 rpm to 500 rpm causes a decrease in the percentage of desulfurization. This is happening because increased stirring speed causes an increase in temperature. The increase in temperature is shown by the temperature indicator on the reactor. As the temperature rises, the hydrogen peroxide oxidizer decomposes, resulting in a drop in the percentage of desulfurization. These findings are in line with the research results of Mohammed and Almilly [11], who tested stirring speeds of 150, 250, 350, and 450 rpm and found that a speed of 350 rpm achieved the highest desulfurization. From the results obtained, the operating conditions of a stirring speed of 300 rpm were chosen which provided the best reactant mixing efficiency and the highest desulfurization results.

4.4 Effect of Residence Time on Desulfurization Percentage

The last independent variable tested is residence time. Residence time is the time required for a substance to react in the reactor before exiting the reactor. The residence time in the ODS process is very important because it affects the effectiveness of the reaction. This study tried variations of residence time for 2, 3, 4, and 5 minutes to find out the best residence time for the Dextrite ODS process. The trendline of the change in residence time to the percentage of desulfurization can be seen in Figure 5.

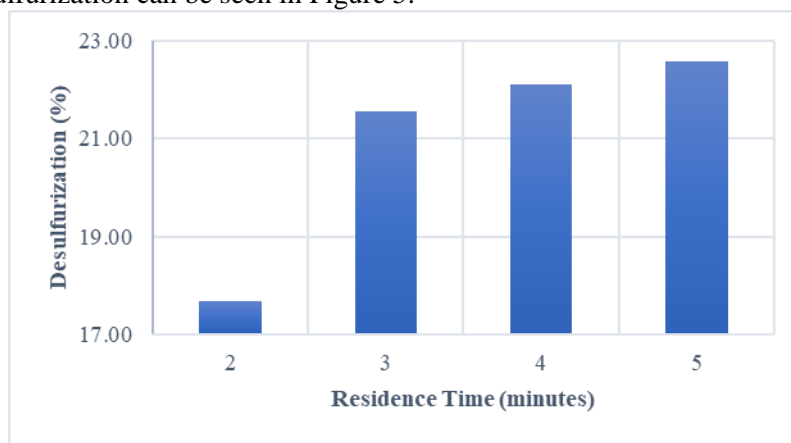


Fig. 5. Effect of Residence Time on Desulfurization Percentage

For the variable residence time, Sample 17 had a lower percentage of desulfurization compared to Samples 18 – 20 because the short residence time caused less efficient contact between the catalyst and diesel fuel. Due to the short residence time, the time needed for the appropriate mixing of the liquid phases is shortened. Making the residence time longer can form more emulsion droplets and increase the interfacial area for reactant contact thereby increasing the overall mass transfer. Better mass transfer increases the conversion of sulfur components in fuel to sulfoxides and sulfones.

Research from de Luna et al. [12] gave the same result, a shorter residence time which was indicated by an increase in flow rate causing a decrease in the desulfurization. This can happen because the high flow rate increases the concentration of diesel fuel in the reactor so that it will require a greater amount of oxidizer, while in the research the amount of oxidizer is a fixed variable. Because of this circumstance, the percentage of desulfurization drops. Therefore, increasing the residence time gradually from 2 minutes to 5 minutes also increased the percentage of desulfurization. It was found that the best operating conditions for this study were at a residence time of 5 minutes which gives the desulfurization of 22.58%.

5. Conclusion

Based on the research that has been done, some conclusions can be concluded as follows.

- The centrifugation-reactor using hydrogen peroxide oxidizer and formic acid catalyst for the ODS process can reduce the sulfur content in Dexlite by 3.36% to 22.58%.
- The best operating conditions of the centrifugation-reactor for the Dexlite ODS process were at 30 °C, a catalyst-fuel ratio of 1:20, stirring speed of 300 rpm, and a residence time of 5 minutes which reduced the sulfur content from 266.78 ppm to 206.55 ppm with a desulfurization percentage of 22.58%.
- In the Dexlite ODS process, increasing the temperature from 30 °C to 70 °C and catalyst-fuel ratio from 1:20 to 1:5 decreases the percentage of desulfurization. Increasing the stirring speed up to 300 rpm can increase the percentage of desulfurization but increasing from 300 rpm to 500 rpm decreases the percentage of desulfurization. Longer residence times from 2 minutes to 5 minutes give a higher desulfurization percentage.

Acknowledgments

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