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The Effect of Complexity of Fuel Oil Composition Compounds on Desulphurization Degrees in Oxidative Desulphurization Processes

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Abstract

Oxidative Desulfurization is an alternative process to reduce sulfur content in fuel. ODS is an oxidation reaction of sulfur compounds in fuel, which contains various hydrocarbon compounds, using an oxidizing agent with the help of a catalyst. The polarity of fuel, sulfur compounds and catalysts is a critical success factor for ODS. This study aims to determine the effect of the complexity of the model fuel used in the ODS process on the degree of sulfur reduction. The complexity variable is considered by polarity, which is determined based on the dielectric constant of the compound using the mixed concentration average of the dielectric constant of the pure compound. The model fuel used in this study is a mixture of hydrocarbon compounds having 6 C atoms in the form of n-hexane, cyclohexane, and benzene. Dibenzothiophena is used as a representative of sulfur compounds with an initial concentration of 300 ppm in each sample. The independent variables that were varied were the composition of the model fuel and the ODS reaction time. Sulfur content in model fuel before and after ODS was analyzed using UV-Vis. Meanwhile, the dielectric constants of fuel and catalyst are determined using empirical equations. The results showed that the polarity of the model fuel changed depending on the composition of the constituent compounds. The ODS process resulted a decrease in DBT levels as a function of increasing the time reaction of ODS. Changes in the polarity of the model fuel solvent give different desulphurization results. The highest degree of desulphurization was obtained at 21% with the use of model fuel with a catalyst which had a dielectrict constant of 1.995.

Keywords: *Oxidative Desulfurization; Polarity; Reduction of sulfur content*

Introduction

The sulfur content in diesel fuel distributed in Indonesia by Pertamina is still at a fairly high level (2000 ppm) when compared to other countries standards like EPA (15 ppm) in America and EURO IV (10 ppm) in Europe (Xie et al., 2020). Sulfur compounds contained in diesel fuel are corrosive which found to react with water at temperatures greater than 80°C, producing acidic compounds (Fang et al., 2008). Emissions of sulfur combustion gas (SOx) have an impact on health and the environment because it triggers acid rain and causes disease in humans by increasing the risk of lung cancer (Rajendran et al., 2020).

Currently, the use of HDS (Hydrodesulfurization) is still the most commonly used method to reduce sulfur content in oil refineries (Ismagilov et al., 2011). This method requires 3 times more catalyst, an increase in temperature of 311 K, and an increase in the need for Hydrogen by 50-100% to completely remove sulfur compounds which of course has a negative impact on the economics of the process (Javadli and De Klerk, 2012).

Oxidative Desulfurization (ODS) method is an alternative in reducing sulfur levels with aromatic chains and is supported by low operating conditions (pressure and temperature) so that it is economically better (Zhao and Baker, 2015). ODS has two major stages, the first oxidizes the sulfur content with the addition of a catalyst so that sulfur, which was originally a non-polar compound will turn into a sulfone or sulfoxide, the second stage, this sulfone or sulfoxide compound which is a polar compound will be separated (Betiha et al., 2018).

ODS studies that have been carried out previously by other researchers using model fuels have obtained convincing desulphurization results of up to 100% (Joskic et al., 2014, Haghighat Mamaghani et al., 2013, Ling and Chen, 2012, Jia et al., 2011). However, when using commercial diesel, a significant reduction in the degree of desulfurization occurs (Az-Zahra et al., 2022, Haruna et al., 2018, Muktaly et al., 2018). The difference between commercial diesel and model fuel is the hydrocarbon compounds used. ODS researchers use model fuels, which are predominantly single hydrocarbon solvents with chains between C5-C8, while commercial diesel carbon chains are longer and more diverse (Haghighat Mamaghani et al., 2013, Ling and Chen, 2012, Jia et al., 2011).

In this study, tests were carried out on various types of solar model complexity variations to determine their effect on ODS performance. The diesel model fuel is varied using a mixture of hydrocarbon compounds found in commercial diesel fractions. According to Frantsina's research in 2020, the diesel fraction contains a mixture of 55% paraffinic

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compounds, 28% naphthenic, and 13% aromatics (Frantsina et al., 2020). By varying the mixture composition of the model fuel, sulfur solvents with different dielectric constants are produced.

The dielectric constant of each hydrocarbon mixture was estimated using the general method of averaging the components of the mixture with a function of solvent concentration (Dumanovic, 1992; Prakongpan and Nagai, 1984; Chien, 1984). The difference in the dielectric constant between the solvent and the catalyst (Δε) becomes a variation which is then tested for its effect on the ODS desulfurization performance.

In this study an analysis of total sulfur content was carried out using the UV-Vis method, because the UV-Vis analysis method has a more accurate final analysis result. The absorbance value from the UV-Vis test of the DBT compound (Dibenzothiophene) shows a strong peak at the maximum absorption wavelength (λmax) of 320 nm (Nejad et al., 2013)..

Methods

In this study, model fuel compounds used short-chain hydrocarbons (C6), namely Hexane, Cyclo-hexane, and Benzene. The chemicals used are analytical grade and are used immediately without prior purification. The DBT (Dibenzothiophene) used was purchased from Sigma Aldrich. Other chemicals, namely n-hexane, Cyclohexane, n-octane, benzene, Formic Acid, and H_2O_2 30%wt were obtained from Merck.

Model fuels whose composition is varied will certainly produce different values of the dielectric constant. Several variations of the composition are carried out as below in Table 1. This solvent variation will later be tested under the same ODS operating conditions to see the comparison.

Table 1 Variations in the fuel composition of the model

Composition Ratio w/w_{total}			
Solvent Code	n-Hexane	Cyclohexane	Benzene
1	1	0	0
2	0.5	0.5	0
3	0.5	0	0.5
4	0.33	0.33	0.33
5	0	1	0
6	0	0.5	0.5
7	0	0	1

Dielectric Constant (ε) Calculation

The degree of polarity is later determined by the dipole moment which is the total vector sum of all the bonds that make up the molecule of the compound as in equation 1.

$$\vec{\mu} = \sum_i q_i \vec{r}_i \quad (1)$$

$\vec{\mu}$ is the dipole moment vector, q_i is the magnitude of the atomic charge i, and $\vec{r}_i$ is the position vector of the atomic charge i. The higher the unbalanced chemical structure, the higher the dipole moment and the easier it is to be polarized in the capacitance test (Rajab et al., 2011). The dielectric constant in the capacitance test is the ratio between the capacitance test (C_x) of a type of solvent and the capacitance test of an empty cell or air (C_0) as in equation 2.

$$\epsilon = \frac{C_x}{C_0} \quad (2)$$

The relationship between dielectric constant and polarity is explained in equations 3 and 4 from the book "Engineering Electromagnetics" (Hayt Jr et al., 2020).

$$\epsilon = \chi_e + 1 \quad (3)$$

$$P = \chi_e \epsilon_0 E \quad (4)$$

Where the value of X_e is a dimensionless value called electric susceptibility and P is polarization. A large dielectric constant value indicates that the compound is susceptible to being polarized in an electric field or capacitance test. The higher the dielectric constant of a compound, the greater the dipole and polar moment of the solvent.

A common analytical method used to estimate the dielectric constant of mixed solvents is to calculate the average of the composition or concentration of the mixture (Dumanovic et al., 1992; Prakongpan and Nagai, 1984; Chien, 1984). The method is formulated by equation 5.

$$\epsilon_c = \emptyset_1 \epsilon_1 + \emptyset_2 \epsilon_2 \quad (5)$$

Where ε_c, Φ_i, and ε_i respectively are the dielectric constant of the mixture, %volume, and the dielectric constant of the pure compound.

ODS Process

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The oxidative-desulfurization (ODS) method is a method of reducing the total sulfur content which oxidizes diesel fuel with the help of an oxidizing agent. This method is also assisted with the help of a catalyst in the desulfurization process so it is called catalytic oxidative-desulfurization (Cat-ODS). In the oxidation stage, diesel fuel containing sulfur will be oxidized to sulfoxide by the oxidizing agent and changed again to sulfone which is more polar and has high solubility in solvents that are not mutually soluble in oil (Sobati et al., 2010).

The ODS activity of the catalyst was tested using a 300 ppm DBT solution as a model fuel. H_2O_2 plays a role as oxidizing agent and propionic acid is used as catalyst. The influence of operating condition parameters which include model fuel composition and ODS reaction time when other parameters are kept constant such as temperature and stirring speed (rpm). First, 1 gram of catalyst, 1 mL of H2O2 and 1 mL of propionic acid were placed in the flask, then stirred using a stirrer at 400 rpm for 5 minutes. Then 10 mL of 300 ppm DBT solution was added, then the flask was closed tightly and stirred at 400 rpm and maintained at 45^{o}C.

UV-Vis Analysis

In this study, the test method used was the UV-Vis SHIMADZU. The compound to be analyzed is DBT, therefore it is necessary to determine the wavelength that will be scanned. The DBT compound (Dibenzothiophene) shows a strong peak at the maximum absorption wavelength (λmax) of 320 nm (Nejad et al., 2013). Therefore, the wavelength range taken is 300-350 nm to get the maximum DBT peak.

The sample resulting from the ODS process is separated from the polar phase by centrifugation. Then the non-polar phase (top layer) was put into a UV-Vis cuvette with a volume of approximately ± 3 mL. The samples were then tested with the SHIMADZU UV-Vis Spectrophotometer owned by the Sustainable Energy laboratory at the Department of Chemical Engineering, University of Indonesia.

Result and Discussion

Effect of Model Fuel Composition on Dielectric Constant

From several variations in composition, it can then be calculated the dielectric constant of each mixture using equation 5. The calculation results are shown in Figure 1.

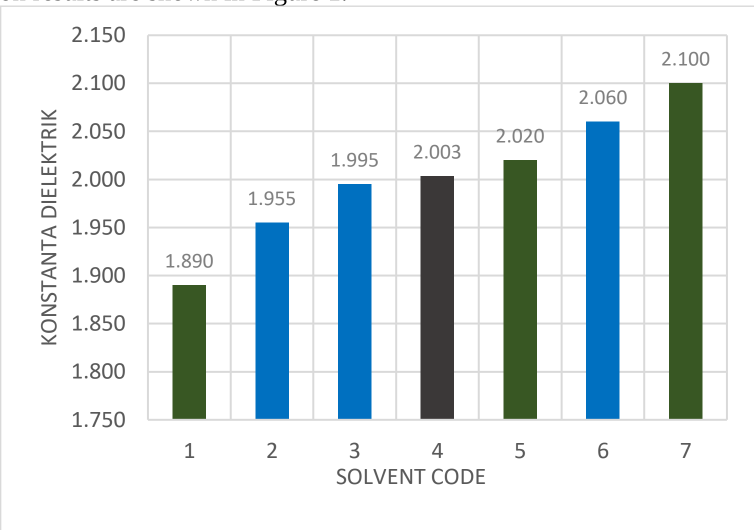

Figure 1. Dielectric Constant Result for Each Solvent Code

These results show that the highest dielectric constant 2.1 is obtained at solvent code 7 with a pure benzene composition. This happens because benzene has the highest dielectric constant of other solvents, which has higher polarity. In solvent code 6, it is a mixed solvent with the highest dielectric constant 2.06 because in this mixture there is a composition of benzene as the majority of its constituents. While the smallest dielectric constant is obtained by solvent code 1 of 1.89 because the majority of its constituents are n-hexane.

Effect of ODS Reaction Time to Degree of Desulfurization

In this section, ODS performance is tested on cyclohexane which has a dielectric constant in the middle, to determine the effect of reaction time on the rate of desulfurization. ODS testing is performed with time variations from 0 to 90 minutes with 4 sample points. The degree of desulfurization is shown in Figure 2.

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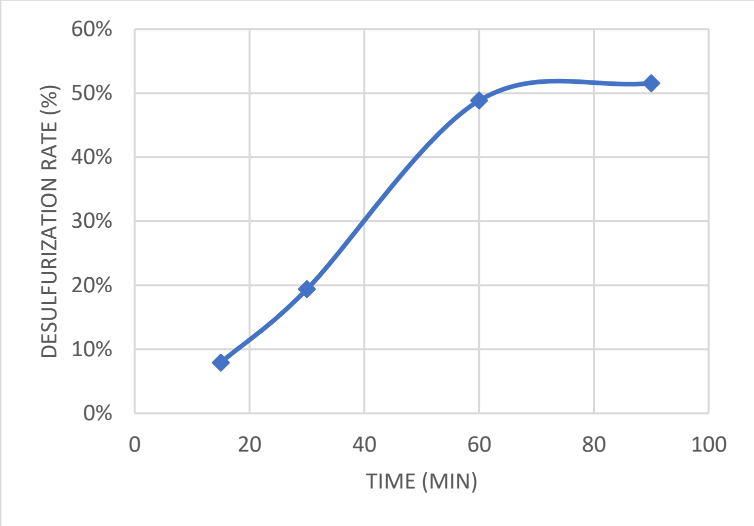

Figure 2. The Effect of ODS Reaction Time to Degree of Desulfurization

From Figure 2, it can be seen that the degree of desulfurization is proportional to the ODS reaction time. But at 60-90 minutes, the increase in the degree of desulfurization is already insignificant and tends to flattening. From it it follows that a good operating time for ODS in this condition is 60 minutes. The highest degree of desulfurization of 52% is achieved in the 90th minute.

Effect of the Dielectric Constant of Solvent on Degree of Desulfurization

The dielectric constant which represents the polarity value of the solvent turns out to have an effect on the degree of desulfurization as shown in Figure 3. The magnitude of the ODS desulphurization start to increases in direct proportion to the dielectric constant. after that the graph reaches a maximum point at a dielectric constant of 1.995 with a desulphurization of 21%. After reaching the maximum point, then the desulphurization decreased gradually until the desulfurization was 8% at a dielectric constant of 2.1.

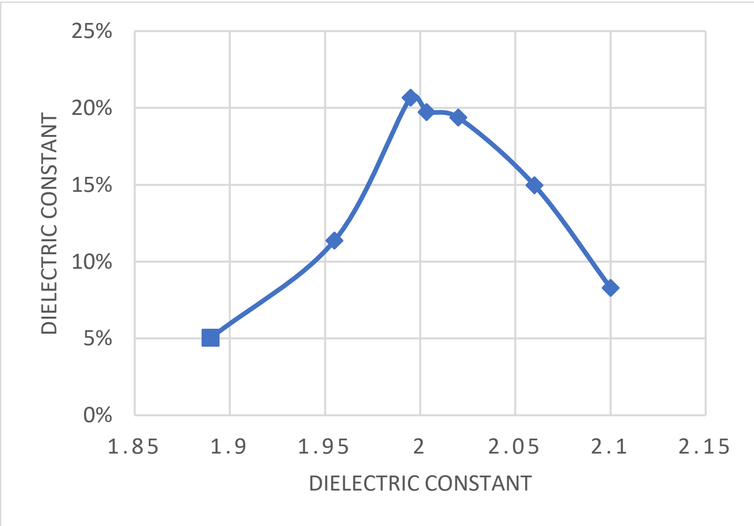

Figure 3. Effect of the Dielectric Constant of Solvent on Degree of Desulfurization

This shows that there is an influence from the model's fuel composition on ODS performance. when viewed from the polarity, initially desulfurization will be directly proportional to the polarity because the catalyst and oxidizer will more easily meet with more polar solvents. This will make the reaction easier to occur.

However, an increase in the polarity of the high solvent will make sulfur, in this case DBT, unable to dissolve properly. This is due to the difference in the polarity of the solvent and the sulfur. In this case Dibenzothiophene which is a hydrocarbon compound with a large aromatic ring system makes it non-polar.

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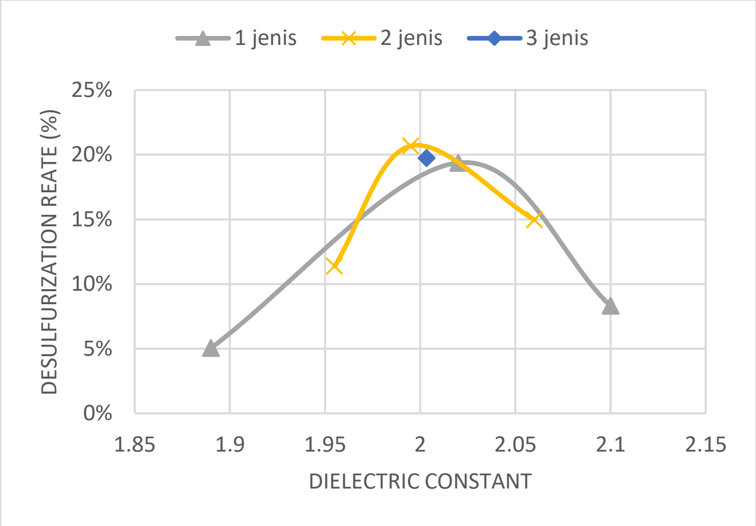

Figure 4. Effect of the Dielectric Constant of Solvent on Degree of Desulfurization by Number of Solvent

Figure 4 shows that the amount of solvent was not fully related to desulfurization. Solvents with one, two, or three types of hydrocarbon components still show the same symptoms when identified using a polarity variable. The three graph plots still show that the highest desulfurization is obtained by solvents with a range of 1.955 to 2.

Conclusion

This research can be concluded as below:

- The composition of the model fuel has an effect on the polarity in terms of the dielectric constant. In order, the polarity of a mixture of hydrocarbons containing more aromatic compounds will be more polar than a mixture with many aliphatic compounds.
- The ODS reaction time has an effect on the degree of desulfurization produced. In the range of 0-60 minutes there was an increase in the degree of desulphurization up to 50%, and tend to flattening after 60 minutes until it reached 52% at 90 minutes.
- Differences in dielectric constant affect the degree of desulfurization. The smaller the difference in polarity of the model fuel constituent and the catalyst, the better desulfurization. However, an increase in the polarity will make desulfurization drop.
- The best ODS Desulfurization was obtained at 21% at the dielectric constant of the 1.995 model fuel with a difference of 55.9 to the catalyst.

Notation Lists

$\vec{\mu}$ = dipole moment vector
q_i = magnitude of the atomic charge i
$\vec{r_i}$ = position vector of the atomic charge i
C_x = Capacitance test of Solvent X
C_0 = Capacitance test of an empty cell or air
X_e = Electric Susceptibility
P = Polarization
ϵ_c = dielectric constant of a mixture
Φ_i = Rasio Volume
ε_i = Dielectric constant of Pure Compound

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