Copper Catalyst in Sulfur Reduction Process with Visible Light

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Abstract

Sulfur gas such as SO_x is one of the harmful residual gases resulting from combustion in vehicle engines due to the high sulfur content in fuel oil, especially diesel. Conventional processes in sulfur reduction still use technology with high process operating conditions and are expensive, thus charging the selling price of low sulfur diesel oil. Light energy is a promising alternative in sulfur reduction process with low production cost. This research will examine the sulfur reduction process with red light assisted by tin catalyst. The results showed that tin catalyst increased the photon energy in red light with sulfur reduction up to 800 ppm in 10 hours. The removal of C-S and O-H groups indicates the formation reaction of $DBTO_2$ after DBT can be cracked from diesel oil hydrocarbon.

Keywords: *Sulfur Reduction, Diesel Oil, Red Light.*

A. INTRODUCTION

Diesel fuel has become a major commodity in the world of transportation, especially heavy vehicles such as buses, trucks and others (Li et al., 2021). Crude oil consists of a wide variety of hydrocarbons and other mixtures containing varying amounts of organosulfuric compounds (OSCs), nitrogen, and oxygen, most of which remain in refined petroleum products including diesel, gasoline, and jet fuel (Abdullah & Xing, 2018; Winkler et al., 2018). The presence of OSCs in such fuels is uninvited due to SOx emissions from their combustion, which are a major cause of global warming, acid rain, and atmospheric contamination, as well as several health problems including respiratory disease, heart disease, and asthma (Rezvani et al., 2018) . In automotive and refining processes, sulfur is also undesirable as it tends to deactivate catalysts and cause corrosion problems in pipes and refining equipment (Chandra; Nanoti, & Madhusudan, 2017). In fuels, sulfur compounds exist in various forms that can be categorized into four main groups, namely mercaptans, sulfides, disulfides, and thiophenes (TH) (C. Liu et al., 2014).

This sulfur can be reduced by sulfur reduction technology called *delsufurization*. Commonly used conventional desulfurization such as *oxidative desulfurization*, *adsorptive desulfurization*, *biodesulfurization*, *extractive desulfurization* as well as *hydrodesulfurization* show capable results to reduce sulfur content (Cerri et al., 2004; Lee Julia A., 2019; Piscopo et al., 2020; Zhang Isabelle; Zhu, Mingming; Zhang, Zhezi; Gao, Jian; Zhang, Dongke, 2022). However, the process used requires a lot of raw materials such as catalysts, additives, adsorbent preparation materials and extractants as well as high operating conditions and long operating times. This needs to be developed to design an alternative process that requires low production costs due to the lack of materials and can take place under mild operating conditions. Suitable energy is light because it is renewable, easily available, can take place in low operating conditions and is environmentally friendly (R. Liu et al., 2018).

One of the energies that can be used is visible light energy. Visible light is light in the range of 400-700 nm that can be seen directly by humans (Zhou et al., 2021). This light is promising because it matches the characteristics mentioned above and has the best safety compared to UV and infrared light (Dadashi-Silab et al., 2021; Gondal et al., 2013). Such as research by Marchese et al. on the carboiodination reaction catalyzed by Pd(0) induced by blue light formed by Lautens groups (Marchese et al., 2022). The catalyst used was $[Pd(allyl)Cl]_2$, the results successfully prepared a series of iodinated hetero- and carbocycles, including *oxindole*, *dihydrobenzofuran*, *indoline*, *chroma*, and *tetrahydronaphthalene*. The reaction system showed a wide tolerance of functional groups, allowing the incorporation of phenol, free carboxylic acid, aniline, and pyridine, among others, into the corresponding products in yields of up to 94%.

Research by Yu et al. revealed a visible light-induced palladium-catalyzed Heck reaction between S,S-functionalized internal vinyl bromide and styrene (Li et al., 2021). In this reaction, various products in moderate to excellent yields were isolated under mild conditions. The resulting diene products can be further converted to highly functionalized trisubstituted furan derivatives

These studies have shown that visible light has a real significant impact for use in chemical reaction processes. This study will conduct sulfur reduction from diesel oil through visible light irradiation under room operating conditions which is new in the world of sulfur reduction. Cu metal is added as a visible light adjuvant to amplify the energy contained therein.

B. METHODS

Diesel oil was taken directly from the Plaju refinery with a sulfur content of 1200 ppm. The visible light used was red light with a wavelength of 700 nm. Cu metal was purchased at Toko Kimia Indonesia. The diesel sample is put into the tube. The tube is placed on the red-light lamp so that the sample will be irradiated by the light from the red-light lamp. The tube and lamp are covered with a metal tube and aluminum foil sheet so that the red light does not come out of the irradiation equipment. It is intended that the irradiation process runs well. After the irradiation process, the sample is removed through the outlet and accommodated in the tank.

C. RESULTS AND DISCUSSION

Desulfurization of diesel oil is an important process in reducing harmful gas emissions such as SOx resulting from fossil fuel combustion. One of the innovative methods used to reduce sulfur content is photocatalytic-based desulfurization with the help of copper (Cu) metal as a catalyst. This process utilizes energy from visible light to activate the catalyst, thereby breaking down sulfur molecules into simpler compounds.

Cu metal acts as a catalyst that accelerates chemical reactions under visible light irradiation. The use of this metal aims to increase the efficiency of sulfur cracking reaction with hydrocarbons in diesel oil, especially when the photon energy intensity is sufficient. The activation of Cu by light generates additional electrons for the beam to accelerate the reaction process.

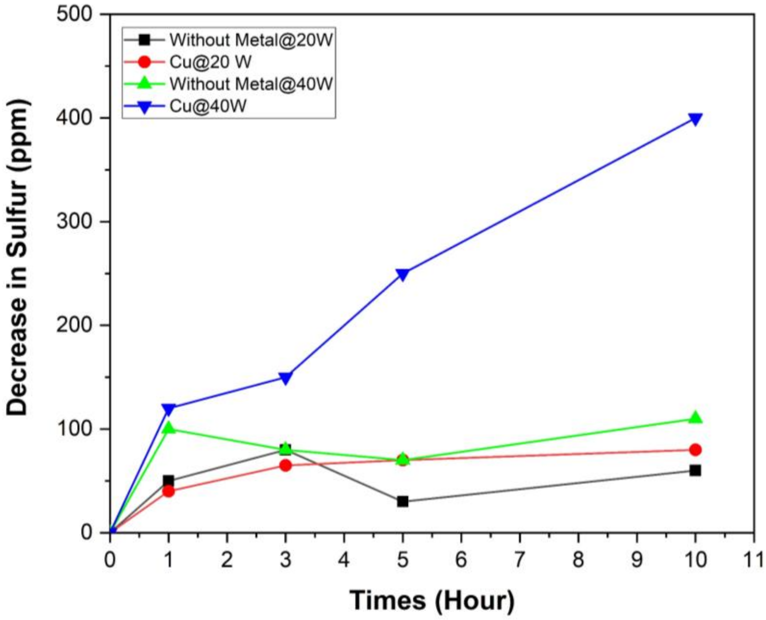

Figure 1. Sulfur Reduction Results of Visible Light Irradiation on Diesel Oil

The sulfur reduction process was carried out using diesel oil with a content of 1200 ppm. The power variations used were 20W and 40 W and the irradiation time was varied from 1 hour, 3 hours, 5 hours, and 10 hours. As shown in Figure 1, the process with no Cu catalyst showed low results compared to using Cu catalyst at both 20W and 40 W power variations. In the metalless condition with 20 W power, the sulfur reduction was very slow and only reached about 50 ppm in 10 hours. This indicates that the photon energy from visible light at low power is not strong enough to break down the sulfur molecules without the help of a catalyst.

In the results without using a catalyst with 20W power, the highest results were obtained at 3 hours with a decrease of 80 ppm while the lowest decrease at 5 hours was 30 ppm. Time 1 hour decreased by 50 ppm and 10 hours by 60 ppm. The use of Cu catalyst at 20W power showed slightly increased results in various time variations where at 1 hour by 40 ppm, 3 hours by 65 ppm, 5 hours by 70 ppm and 10 hours by 80 ppm which is the highest sulfur reduction in this variation.

In the 40 W power variation the results are not much different from without the use of catalysts where at 1 hour it is 100 ppm, at 3 hours it is 80 ppm, at 5 hours it is 70 ppm, and 10 hours it is 110 ppm. The results increased dramatically when using Cu catalysts where at 1 hour the decrease was 120 ppm, this result continued to increase along with the length of irradiation time used where at 3 hours it became 150 ppm, at 5 hours it became 250 ppm and at 10 hours it increased dramatically to 400 ppm which is the highest result in this study.

From the sulfur reduction results, the process without catalyst showed low and fluctuating results compared to using Cu catalyst. The use of Cu catalyst increases the yield drastically and linearly as the power used increases and the length of irradiation time results in increasing sulfur reduction. To study the increase in sulfur reduction results due to the use of Cu catalyst, it is necessary to analyze the changes that occur in visible light.

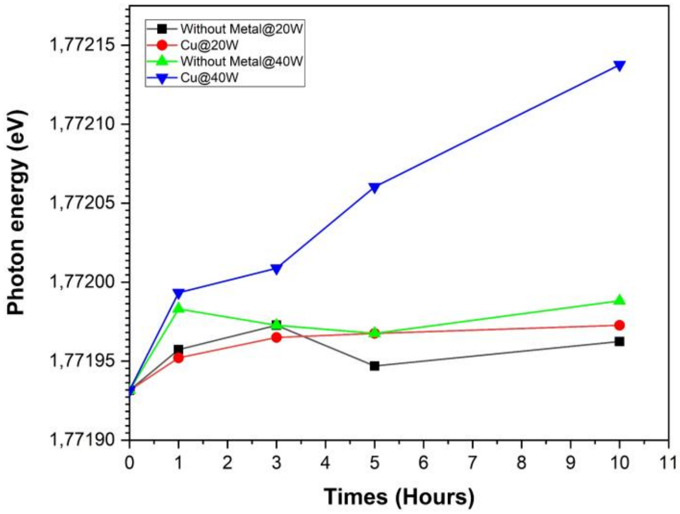

Figure 2. Changes in Photon Energy Due to the Use Without and with Metals in the Sulfur Reduction Process of Diesel Oil

In light there is energy that composes it which is referred to as photons. Photons are a set of electrons that move in the light. The energy of photons delivered by visible light is calculated using the Planck equation, ($E = hc / \lambda$) with a wavelength of 700nm (Qian, 2023; Wang & Hu, 2014) . These electrons can be increased by being supported by Cu metal by donating its electrons so that in visible light there is an increase in electrons which causes the photon energy to increase. As shown in Figure 2, the results are in line with the results of sulfur reduction where the highest results were achieved at a power variation of 40 W and the longest irradiation time at 10 hours with the use of Cu catalyst with the highest photon energy of 1.772138 eV compared to the initial photon energy of 1.771931 eV which is an increase of 0.000206 eV. This high power is related to the higher beam intensity as well. Higher irradiation power produces greater light intensity, so the number of available photons also increases. This will make it easier for the light to make the electrons on Cu detached so that the photon energy will also increase. This will strengthen the ability of the light to break down sulfur molecules in diesel oil more efficiently.

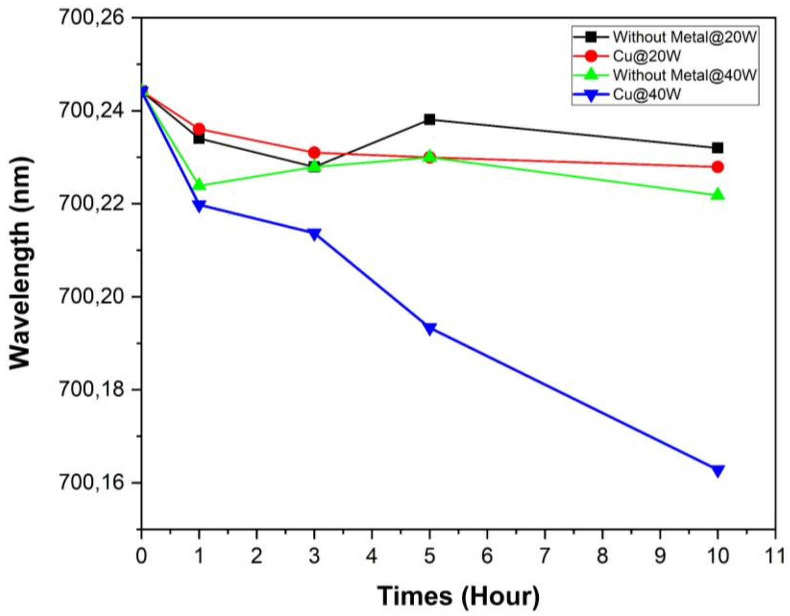

Figure 3. Decrease of Visible Wavelength in Diesel Oil Sulfur Reduction Process

Wavelength is inversely proportional to photon energy. The greater the photon energy produced makes the wavelength of the beam smaller. This is because high photon energy indicates that the movement of the electrons in the beam is also getting higher which causes the speed of the beam to increase, so that the distance traveled by the beam is getting shorter which is shown by the shrinking wavelength. The most significant results are shown in Figure 3 where the 50W power variation using Cu catalysts shows a decreasing wavelength with the smallest wavelength at a time variation of 10 hours of 700.1628 nm from the initial 700.2442 nm. The average wavelength in this study is 700.2219 nm.

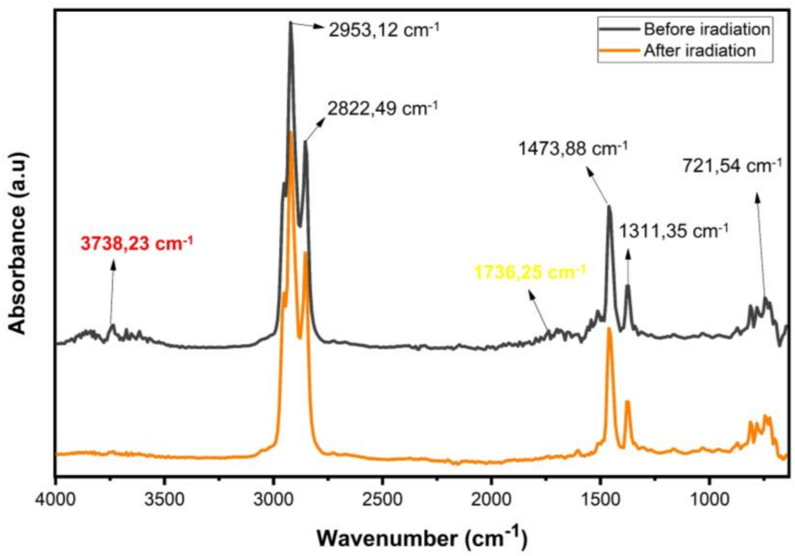

Figure 4. Results of FTIR Analysis of Diesel Oil Before and After Visible Light Irradiation

To prove the changes in the compounds contained in diesel oil, FTIR analysis was conducted to see the changes in functional groups before and after the irradiation process. FTIR spectra of diesel oil before and after visible light irradiation showed significant changes in some relevant peaks as shown in Figure 4, reflecting changes in chemical composition. Before irradiation, a peak at 3738.23 cm^{-1} was observed indicating the presence of hydroxyl groups (O-H), possibly derived from oxygen compounds. In addition, the peak at 1736.25 cm^{-1} indicates a C-H group present in sulfur compounds. These two groups are the main indicators of sulfur compounds in diesel oil. There are also peaks at 2953.12 cm^{-1} and 2822.49 cm^{-1} derived from aliphatic C-H stretching vibrations, as well as peaks at 1473.88 cm^{-1} and 1311.35 cm^{-1} indicating deformation of methyl ($-CH_3$) and methylene ($-CH_2-$) groups. In addition, the peak at 721.54 cm^{-1} is attributed to rocking vibrations of methylene groups in long chain hydrocarbons.

After irradiation, the peaks at 3738.23 cm^{-1} and 1736.25 cm^{-1} disappear completely, indicating that the hydroxyl groups and sulfur compounds have been degraded or removed during the irradiation process. This indicates the success of the diesel oil desulfurization process using visible light. In addition, the peaks at 2953.12 cm^{-1} and 2822.49 cm^{-1} show a slight decrease in intensity, indicating a small change in the structure of aliphatic hydrocarbons. The peaks at 1473.88 cm^{-1} and 1311.35 cm^{-1} remain with minimal intensity changes, indicating that most of the hydrocarbon structures remain stable. Meanwhile, the peak at 721.54 cm^{-1} is also still detected, indicating the stability of the long chain hydrocarbon structure.

D. CONCLUSION

The process of sulfur reduction with visible light is promising because the process is lightweight in terms of production, process conditions and friendliness to the environment and human health, making it easier to control if applied to industry. This process shows the success of reducing sulfur with diesel oil using Cu-assisted visible light where the higher the power and irradiation time used will produce a high sulfur reduction as well, in this case at 10 hours and 40W power with a decrease of 400 ppm. This result is proven by the loss of sulfur compound constituent groups, namely C-S and the loss of O-H groups representing oxygen, which indicates the formation of sulfonate compounds that are more easily separated than the initial sulfur compounds such as BT, DBT, 4,6-DMDBT.

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