Article

Oxidative Desulfurization of Real High-Sulfur Diesel Using Dicarboxylic Acid/H$_2$O$_2$ System

Barham Sharif Ahmed [1], Luqman Omar Hamasalih [1], Kosar Hikmat Hama Aziz [1,2,*], Khalid M. Omer [1] and Iqrash Shafiq [3,4]

1   Department of Chemistry, College of Science, University of Sulaimani, Qlyasan Street,
    Sulaimaniyah 46001, Iraq
2   Department of Medical Laboratory of Science, College of Health Sciences, University of Human Development,
    Sulaimaniyah 46001, Iraq
3   Catalysis & Reaction Engineering Research Group, Department of Chemical Engineering,
    COMSATS University Islamabad, Lahore Campus, Defence Road, Off Raiwind Road, Lahore 54000, Pakistan
4   Refinery Division, Pak-Arab Refinery Limited "Company" (PARCO), Corporate Headquarters,
    Korangi Creek Road, Karachi 75600, Pakistan
*   Correspondence: kosar.hamaaziz@univsul.edu.iq

Abstract: From the perspective of pollution, economics, and product quality, it is very important to find an efficient way to minimize the sulfur content of petroleum products such as gasoline and diesel. In this work, an effective, inexpensive, and simple oxidative desulfurization system based on hydrogen peroxide activation by three dicarboxylic acids which have different carbon numbers (i.e., malonic acid, succinic acid, and glutaric acid) was utilized for the desulfurization of a real diesel sample with high organic sulfur-containing compounds. The desulfurization process was based on the oxidation of sulfur compounds in diesel fuel to the corresponding sulfones followed by acetonitrile extraction of the sulfones. To select the optimal experimental conditions, the effects of several parameters, including temperature, catalyst H$_2$O$_2$ dosages, and treatment time, were investigated. The results showed that the developed system was effective in desulfurizing real diesel fuel with high sulfur content. With an initial total sulfur content of about 8104 mg/L, the desulfurization rate from the diesel sample reached more than 90.9, 88.9, and 93%, using malonic acid, succinic acid, and glutaric acid, respectively. The optimum parameters such as reaction temperature, reaction time, H$_2$O$_2$ (50 w/w%), and carboxylic acid dosage for oxidative desulfurization were determined to be 95 °C, 6 h, 10 mL, and 0.6 g, respectively. The conversion of refractory sulfur compounds into extractable sulfone forms was verified using gas chromatography. Moreover, the kinetic study confirmed that the designed reaction system follows the pseudo-first-order kinetic model.

Keywords: glutaric acid; hydrogen peroxide; high sulfur diesel; malonic acid; oxidative desulfurization; succinic acid

1. Introduction

Energy supply and environmental pollution are now two of the main topics of public concern due to economic development and population growth. Widespread consumption of fuel products by various sectors produces a huge variety of pollutants that can pose a serious threat to human health and the environment [1]. Sulfur dioxide, a toxic gas produced during the burning of sulfur-containing fuels like coal and diesel, is harmful to both humans and the ecosystem. Furthermore, sulfur dioxide reacts with moisture, resulting in acidic rain and low pH fogs. Acid rain causes building erosion, changes the pH of soil and water, and harms aquatic life [2]. Therefore, the production of green diesel fuel has shown great potential to ensure the environment remains healthy and free from pollution [3,4]. Elimination of sulfur-containing compounds is an essential process in petroleum refining and can be developed through several catalytic oxidative or adsorption processes

at optimized operational conditions [5]. Desulfurization of fuel oils with high sulfur content could mitigate the environmental risk of harmful gases in the atmosphere. From the perspective of environmental pollution, economics, product quality, and stringent environmental regulation, it is very important to develop an efficient desulfurization method for petroleum products such as gasoline and diesel. Desulfurization processes have been extensively investigated using various techniques such as hydrodesulfurization [6,7], extraction with deep eutectic solvents [2], oxidative desulfurization [8,9], and adsorptive desulfurization [10]. These methods appear to be the most promising for effective desulfurization of diesel fuel. Numerous studies regarding desulfurization of petroleum products, such as model and real diesel, have been reported in the literature using methods such as extractive desulfurization with 1-butyl-3-methylimidazolium tetrafluoroborate [11]; adsorptive desulfurization of model diesel fuel by selective adsorption on activated carbons [12,13]; desulfurization on various adsorbents including activated alumina [14], zeolites [15], and Zn-impregnated montmorillonite clay [16]; oxidative desulfurization based on hydrogen peroxide promoted by formic acid and catalyzed by activated carbon [17]; nanoporous activated carbons [18]; bimetallic and trimetallic oxides doped on molybdenum oxide [19]; bimetallic nanoparticles loaded on activated carbon [20]; various types of deep eutectic solvents [21–23]; ionic liquid-based PMoO catalysts and recyclable NaClO oxidant [24]; dual Brønsted acidic deep eutectic solvents [25]; and meso/macroporous $H_3PW_{12}O_{40}/SiO_2$ catalyst with high specific surface areas at room temperature [26]. Among the studied techniques, oxidative desulfurization processes are considered to be one of the most promising methods for desulfurization because of characteristics such as simple processing and high desulfurization efficiency.

In the oxidative desulfurization system, refractory sulfur compounds in fuel feedstocks are sequentially oxidized to produce sulfones (first to the sulfoxide, then to sulfone). Sulfones are formed when oxidants chemically convert their reactive oxygen species to sulfone compounds [27], and the produced sulfones are separated by solvent extraction. Oxidative desulfurization appears to be a promising process because it has many potential advantages. These include not needing hydrogen, mild operating conditions, and high reactivity of the most refractory sulfur-containing compounds, such as dibenzothiophene and its alkylated derivatives, to oxidation [28]. Moreover, because of their high polarity, oxidized sulfur-containing compounds such as sulfones and sulfoxides can easily be removed by solvent extraction or selective adsorption.

Recently, oxidative desulfurization technologies have received increasing attention for the treatment of diesel fuels. Carbon-supported heteropoly acids have shown effective catalytic activity for oxidative desulfurization of model diesel fuel containing dibenzothiophene and heptane by 30% H_2O_2 [29,30]. Timbila and coworkers used ionic liquid (1-butyl-3-methyl imidazolium hydrogen sulfate [BMIM][HSO4]) as a solvent and catalyst and, in the presence of the oxidant H_2O_2, for oxidative desulfurization of biodiesel to achieve a maximum sulfur removal of 43% after two hours [31]. The same ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO4]) with N-butylpyridinium hydrogen sulfate ([C4Py][HSO4]) as an extractant and catalyst has been investigated for desulfurization of diesel [32]. A biomimetic catalytic system was developed for aerobic oxidative desulfurization that couples Mo7 POM with deep eutectic solvents based on carboxylic acids. It was found that the desulfurization efficiency was closely connected to the reaction energy barrier of organic acid oxidation in deep eutectic solvents rather than to conductivity, viscosity, or hydrogen-bonding strength [33]. Andevary and coworkers synthesized the Lewis acidic ionic liquid of 1-octyl-3-methylimidazolium tetrachloroferrates ([Omim]FeCl$_4$) and introduced it for extraction/oxidative desulfurization of model and real diesel fuels by using H_2O_2 as an oxidizing agent. The results revealed that [Omim]FeCl$_4$ was able to desulfurize two real diesel fuels containing 590 and 2573 ppm of sulfur with an efficiency of 85% and 61.2%, respectively. Rafiee et al. [34] synthesized carbon polyoxometalate containing $H_5PMo_{10}V_2O_{40}$ via hydrothermal treatment with an aqueous solvent from natural potatoes as a green, synthetic method for oxidative desulfurization of diesel.

The catalyst showed a strong ability to remove sulfur from model and real oil. $LaVO_4$ photocatalyst prepared using the hydrothermal approach was investigated in oxidative desulfurization of diesel pool fractions and diesel oil blends [9]. Banana-peel-derived activated carbon was impregnated with copper and nickel to create Cu/AC- and Ni/AC-supported catalysts. The prepared catalysts were applied in combination with NaClO oxidant for the oxidative desulfurization of dibenzothiophene under extremely mild operating conditions [35]. Oxidative desulfurization of real diesel has also been successfully examined using molybdenum-anchored metal-organic frameworks [36], Nano core-shell SiO_2@V-PIL catalysts [37], Magnetic catalytic composites based on ZiF-8 support [38], and homogeneous and SBA-15-supported peroxophosphotungstate catalysts [39]. These procedures are effective and could be used to desulfurize real diesel with great efficiency. However, most of these catalysts require time-consuming preparation and are expensive, scarce, and hazardous to the environment, which limits their use in oxidative desulfurization. As a result, developing a low-cost, easy-to-use oxidative desulfurization system is extremely desirable.

Herein, an oxidative desulfurization process following simple solvent extraction has been developed and investigated for untreated high-sulfur diesel fuel (8104 mg/L of total sulfur content). It utilizes three dicarboxylic acids (malonic acid, succinic acid, and glutaric acid) as H_2O_2 activators. The effects of various operating parameters, including treatment time, reaction temperature, and the oxidant/catalyst dosages, on the oxidative desulfurization efficiency were studied. Furthermore, the conversion of refractory sulfur compounds into the corresponding extractable sulfone and sulfoxide compounds during the treatment processes was confirmed based on the results of gas chromatography analysis.

2. Material and Methods

2.1. Materials

The untreated real diesel fuel (initial sulfur content of 8104 mg/L) used in this study was obtained from the Petrol station, Sulaymaniyah-Iraq. The selected dicarboxylic acids (malonic acid (99% purity), succinic acid (99% purity), and glutaric acid (99% purity)), were purchased from Merck. Liquid hydrogen peroxide (50% *w/w*) and acetonitrile (≥99% purity) were purchased from Biochem.

2.2. Desulfurization Activity Testing

A lab-scale oxidative desulfurization system was designed as shown in Figure 1. The process was conducted in a 250 mL round-bottom flask in a batch mode. After heating the hot plate, untreated diesel oil (50 mL) with an initial total sulfur content of 8104 mg/L was added to the round-bottom flask, and during the experiment, the temperature was maintained at 95 °C. The solution of H_2O_2 (10 mL, 50% *w/w*) and selected dicarboxylic acid (malonic acid, succinic acid, or glutaric acid) catalyst (0.6 g) were added to the flask under stirring conditions (1100 rpm) for the desired time. After the completion of the reaction, the mixture was cooled to room temperature and separated between the catalyst and water. Separation of sulfone and sulfoxide compounds from the oxidized diesel layer after oxidation was carried out with acetonitrile via the reflex process in a 1:1 ratio. The gas oil–solvent mixture was stirred at 1000 rpm for 70 min at 50 °C, after which the two layers were separated using 250 mL separation funnels. The total sulfur content of gas oil before and after the ODS treatment was determined using energy disperse X-ray fluorescence and GC-PFPD. Each test was repeated twice, and the average results were reported.
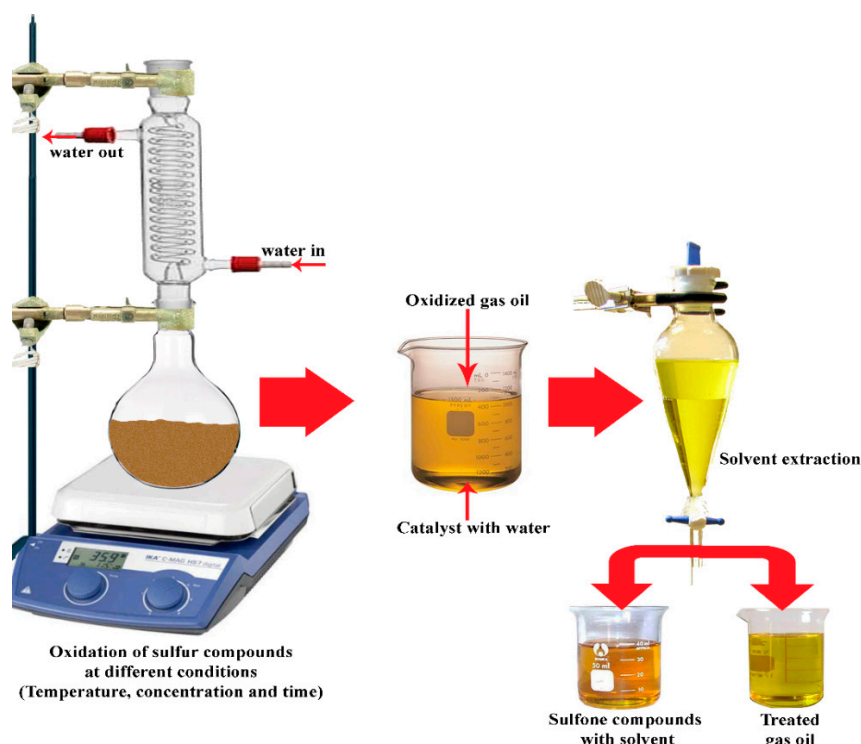
Figure 1. Schematic diagram of the reaction setup.

2.3. Analysis of Real Diesel

The total sulfur content of real diesel samples was measured based on the ASTM D4294 method usingthe Sulfur-in-Oil Analyzer (model NEX QC, Energy Dispersive X-Ray Fluorescent (ED-XRF) spectrometer). The ED-XRF spectrometer was calibrated with five liquid calibration standards. The transformation of sulfur compounds into extractable sulfone products after the oxidative desulfurization process was confirmed using gas chromatography. An Agilent (GC: 6890, MS: 5975) was equipped with a capillary column DB-5MS (10 m × 0.25 mm ID × 0.1 μm film thickness). The carrier gas was helium at a flow rate of 6.0 mL/min. The IR spectra were recorded on a Perkin-Elmer FT/IR spectrometer in the (400–4000 cm^{-1}) range using KBr pellets (νmax in cm^{-1}) from the UK.

3. Results and Discussion

3.1. Oxidation Desulfurization of Real Diesel

The oxidative desulfurization reaction is thought to be a two-step process. In the presence of an oxidant, bivalent sulfur is first oxidized to the hexavalent equivalent sulfone. It involves adding two oxygen atoms to sulfur without breaking any carbon–sulfur bonds; a sulfoxide molecule is formed as an intermediate. Under appropriate conditions (i.e., excess of oxidant), sulfones are formed, and no sulfoxide remains in the medium. H_2O_2 is a frequently used oxidant that is both ecologically safe and stable. When H_2O_2 reacts with carboxylic acid, organic peracids are produced. The −COOH group in the dicarboxylic acid is easily oxidized into peroxycarboxyl groups by H_2O_2. Figure 2 shows the mechanism of the oxidative desulfurization process by dicarboxylic acid. Then a purification step can be performed using liquid–liquid extraction for the separation of oxidized sulfur compounds.
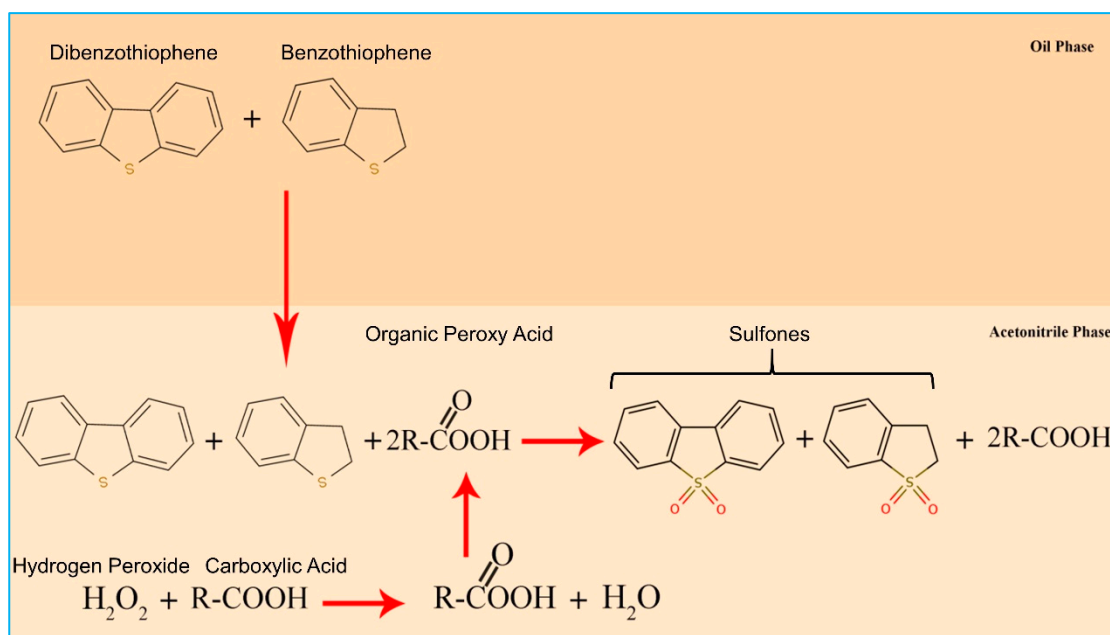
Figure 2. Reaction pathway of oxidative desulfurization catalyzed by dicarboxylic acids.

Herein, untreated diesel with a total sulfur content of 8104 mg/L was chosen as a fuel source to appropriately test the performance of the applied oxidative desulfurization method. The characteristics of tested diesel fuel before and after the oxidative desulfurization process are shown in Table 1. Three dicarboxylic acids were used as hydrogen peroxide activators in the desulfurization process. The combination of H_2O_2 and the selected dicarboxylic acid produces peracids (RCOOOH), which subsequently react with the sulfur component in the diesel sample to make the appropriate sulfone and water as a byproduct [8].

Table 1. Evaluation of diesel oil fractions before and after treatment.

Test	Results before Treatment	Results after Treatment
Specific gravity@ 15.6 °C	0.826	0.809
API gravity	39.8	43.4
Flashpoint °C	67	68
Pour point °C	−11	−13
Vis.@50 °C/Cst	2.18	2.09
%Sulfur content	0.8104	0.057
Distillation		
Initial B.P °C	171	180
Vol. at %10	195	209
Vol. at %50	256	252
Vol. at %70	292	282
Vol. at %90	336	320

3.2. Effect of Parameters on Desulfurization Efficiency

3.2.1. Influence of Time on Reaction

To determine the influence of time of reaction, temperature, the dosage of selected dicarboxylic acids, and H_2O_2 on the oxidative desulfurization efficiency, various desulfurization experiments were carried out on real diesel under different operating conditions. Figure 3 shows sulfur removal as a function of treatment time. As shown in this figure, the results are improved by increasing the initial reaction time and then slightly decreasing it. This can be explained by describing the interaction of oxidants over time. H_2O_2 and dicarboxylic acid can interact with sulfur compounds to produce sulfoxides and sulfones.

This reaction, like any other chemical reaction, requires enough time to complete and develop over time. The best results are observed within 6 h of treatment. After this time, the desulfurization rate does not increase with time, which means that there is an optimal time for the oxidation system. Although it can be seen that after the optimal value, as the time before the desulfurization rate decreases, its decrease is not at all obvious. This reduction in sulfur removal is due to the loss of perdicarboxylic acid and hydrogen peroxide, and their decomposition accelerate the conversion of the oxidized sulfur compound to sulfone.
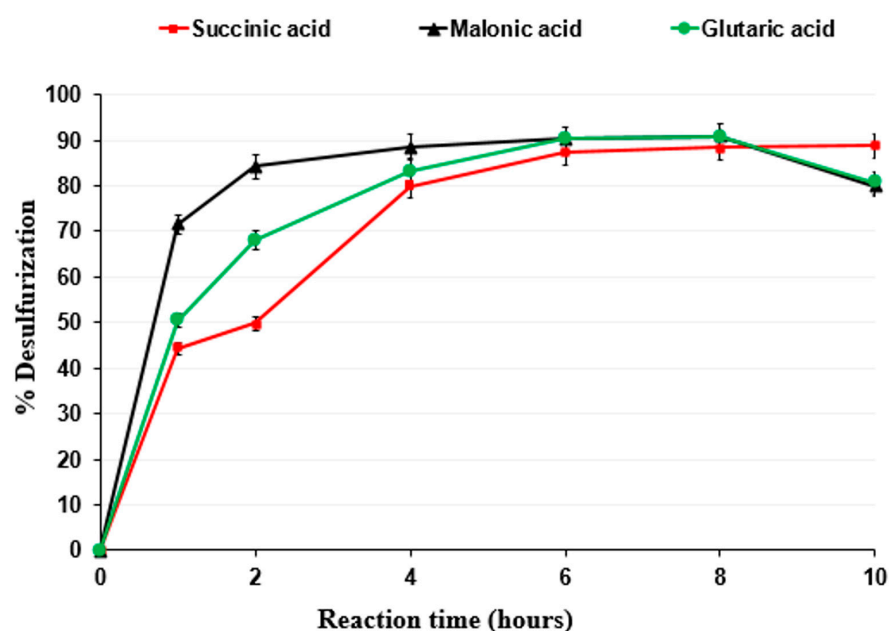

Figure 3. Oxidative desulfurization processes of real diesel. Reaction conditions: sulfur content: 8104 mg L^{-1}; dicarboxylic acid loading: 0.6 g; H_2O_2 with 50% *w/w*: 10 mL.

3.2.2. Effect of Temperature on Desulfurization Efficiency

An important step in reducing operating expenses and improving reaction catalytic efficiency is optimizing the catalyst, H_2O_2, and energy usage. The effect of temperature on the desulfurization rate was evaluated across the range of 50–125 °C, as shown in Figure 4. The results indicated that the efficiency of the process is strongly dependent on temperature; the reaction proceeds completely with the increase of oxidation temperature. At low temperatures, the actions may not have sufficient thermal energy to reach thermodynamic equilibrium. The results show that the desulfurization rate decreases with a temperature above 110 °C; this may be due to decomposition of oxidizing components. Furthermore, the quality of the diesel can also change as the temperature rises due to a streak of valuable volatile components in the diesel. In addition, as the temperature increases, unsaturated components can be oxidized and cause the consumption of part of the oxidizing agent. Therefore, the optimum temperature of the developed system was selected to be 95 °C.
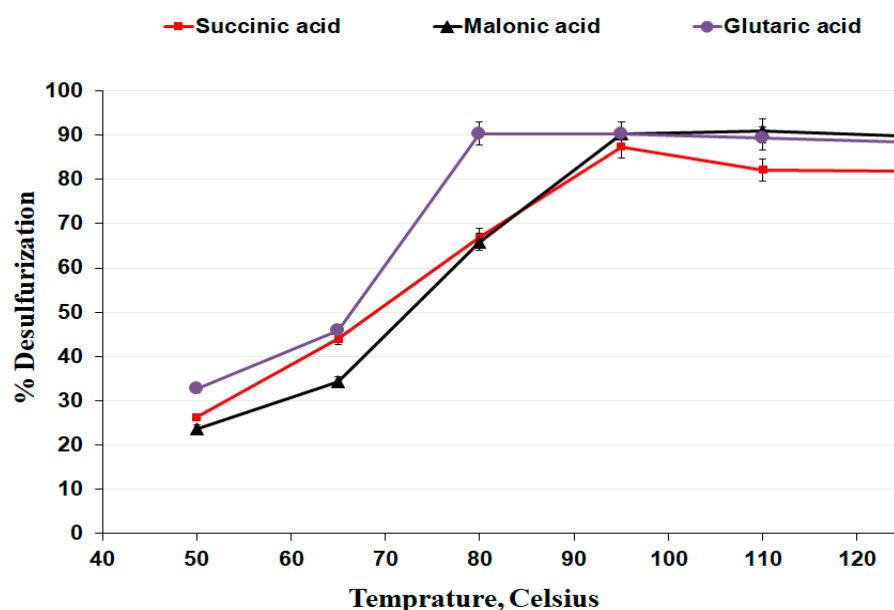
Figure 4. Effect of reaction temperature on the oxidative desulfurization processes. Reaction conditions: initial sulfur content: 8104 mg L^{-1}; treatment time: 6 h; dicarboxylic acid dosage: 0.6 g; H_2O_2 (50% *w/w*): 10 mL.

3.2.3. Effect of Dicarboxylic Acid Dosage

Figure 5 shows the effect of dicarboxylic acid dosage on the desulfurization process whenthe reaction temperature and time were kept constant at values of 95 °C and 6 h, respectively. As expected, the conversion of organosulfur compounds was greatly promoted by increasing the amount of catalyst. The results showed an improvement in sulfur reduction by increasing the catalyst dosage from 0.1 to 0.6 g, increasing the desulfurization rate from 68.5, 67.5, and 84% to 90.3, 87.39, and 90.2% by weight, using malonic, succinic and glutaric acid, respectively. Further increasing the dicarboxylic acid dosage did not remarkably increase the conversion rate.
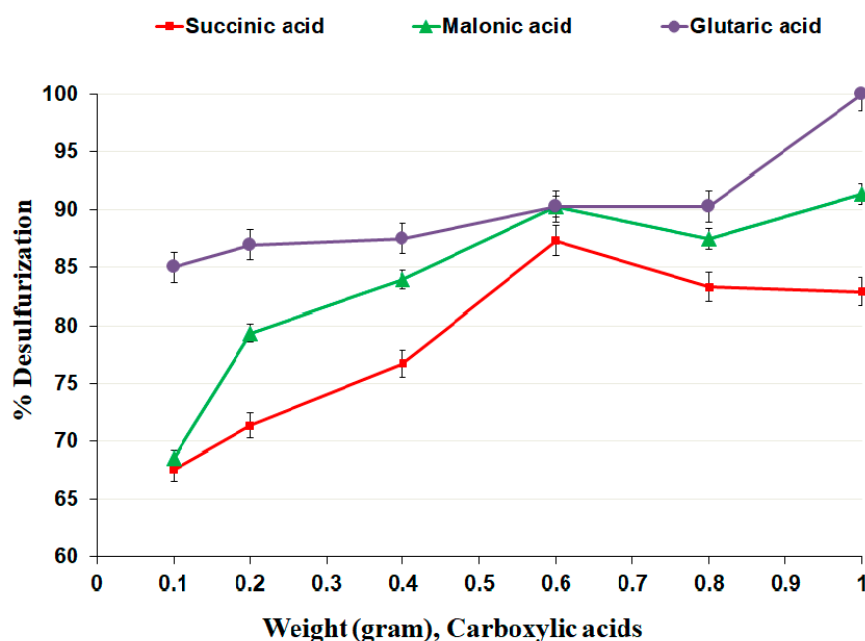

Figure 5. Optimization of dicarboxylic acid loading for oxidative desulfurization. Reaction conditions: sulfur content: 8104 mg L^{-1}, temperature: 95 °C, reaction time: 6 h.

3.2.4. Effect of Hydrogen Peroxide Dosage

The effect of hydrogen peroxide (H_2O_2) on sulfur removal is shown in Figure 6. Sulfur removal initially increases as the ratio of oxidant to sulfur-containing compound increases (i.e., the ratio of hydrogen peroxide to organic sulfur compound). Beyond a certain value, the quantity of oxidant no longer has a significant influence on desulfurization, which could be attributed to excessive oxidant, i.e., hydroperoxide adsorption for H_2O molecules on the accessible active sites of the carboxylic acids, consequently dropping the adsorption of organosulfur compounds [40,41]. The best desulfurization results were obtained with 20 mL of the oxidant for glutaric acid, which produced a desulfurization rate of 92.3 wt%. Increasing the oxidant level above 20 mL did not affect the desulfurization rate.
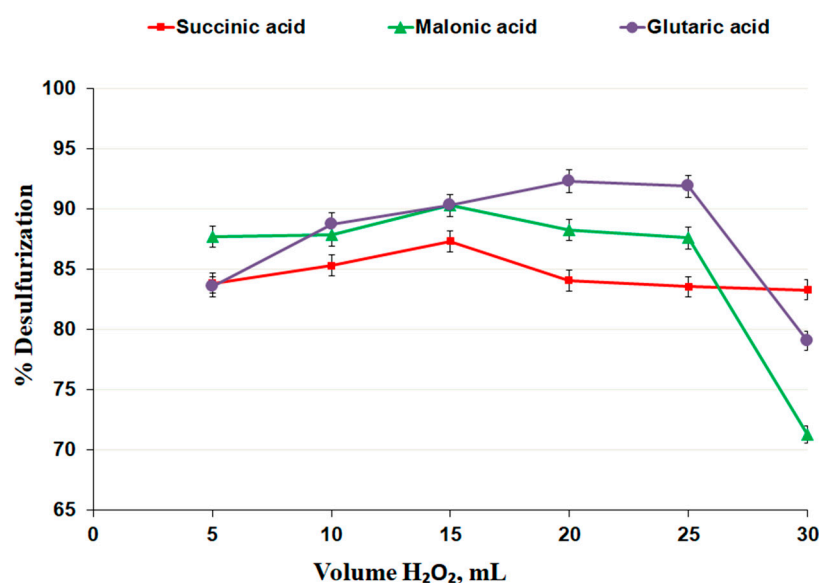
Figure 6. Optimization of H_2O_2 (50 $w/w\%$) addition for oxidative desulfurization. Reaction conditions: sulfur contents: 8104 mg L^{-1}; dicarboxylic acid loading: 0.6 g; reaction temperature: 95 °C; reaction time: 6 h.

3.3. Characterizations of Treated Diesel

Gas chromatography was used to confirm the transformation of refractory sulfur compounds into extractable sulfones. Some of the sulfur compounds have been identified by comparing the real diesel chromatogram with standard common sulfur-containing organic compounds. As shown in the chromatogram in Figure 7, the identified sulfur compounds significantly decreased after oxidation (Figure 7A,B) and completely disappeared after extraction with acetonitrile (Figure 7C). These chromatographs show that virtually all the sulfur-containing compounds in the real diesel sample were oxidized to their corresponding sulfones after oxidative/extractive treatment.

The composition of the diesel oil before oxidation was characterized by IR spectroscopy, and the result is shown in Figure 8A. The aliphatic CH tract is between 2956 cm^{-1} and 2855 cm^{-1} due to the extension of the CH$_3$ groups. While the CH$_2$ bands appear at 2924 cm^{-1}, the bending vibration of the symmetrical methyl appears at 1377 cm^{-1}, and the methylene bending occurs at 1463 cm^{-1}. Figure 8C shows the IR spectrum of gas oil after oxidation. In these spectra, the sulphone bands with symmetrical and asymmetric elongation were observed at 1158 cm^{-1} and 1307 cm^{-1}, respectively. This indicated that the organic sulfur compound was converted to the corresponding sulfone, which has higher polarity. It also indicated that these sulfones were effectively removed from the oxidized diesel layer by acetonitrile after solvent extraction, as shown in Figure 8C.
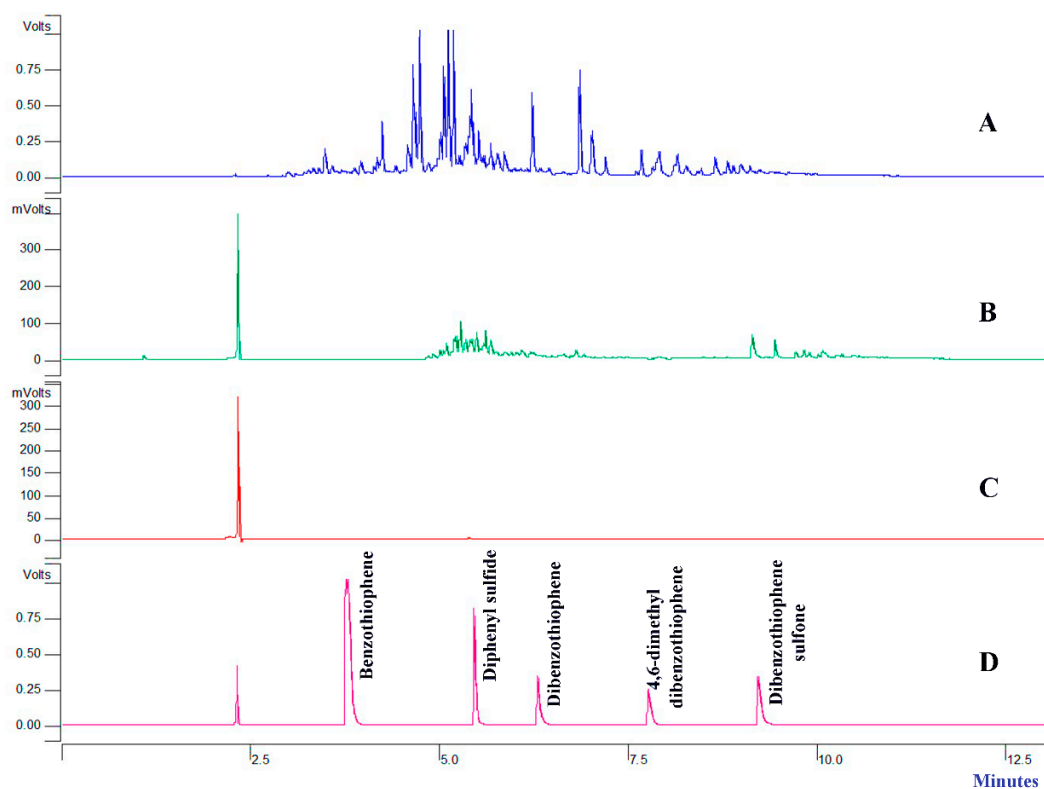
Figure 7. GC-PFPD for real diesel. (**A**) untreated diesel, (**B**) after oxidative treatment, (**C**) after extraction with acetonitrile, and (**D**) standard sulfur compounds.
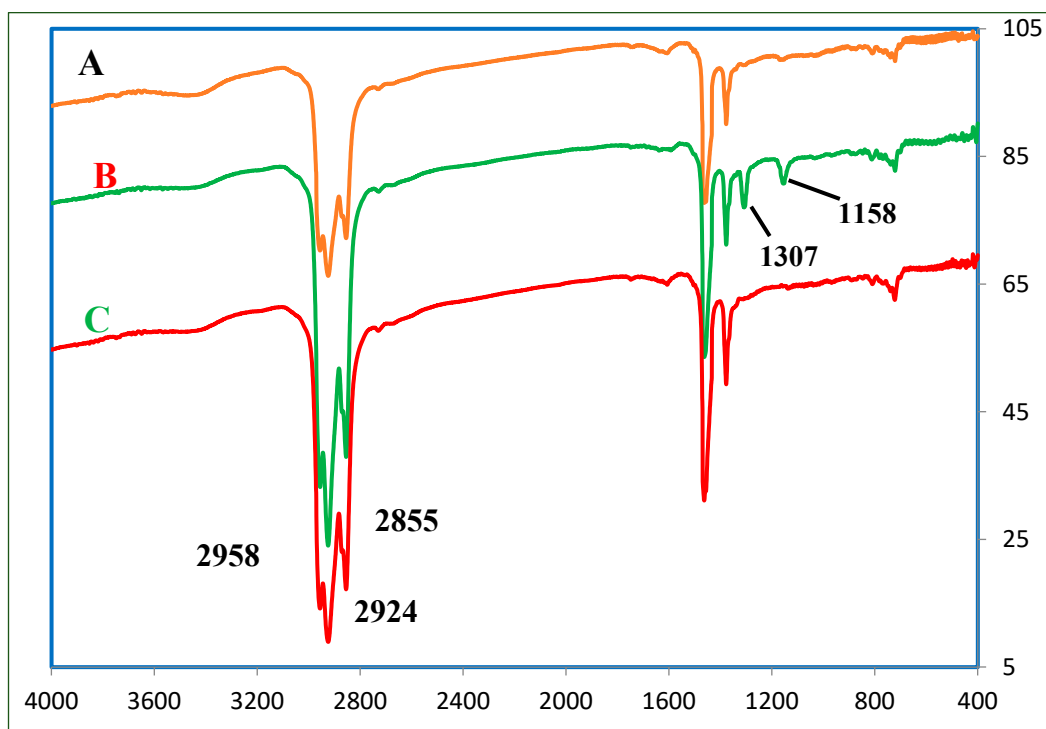

Figure 8. FTIR spectrum for diesel oil. (**A**) before oxidation, (**B**) after oxidation, and (**C**) after extraction by acetonitrile.

3.4. Kinetic Study

The real diesel comprising 8104 mg L^{-1} of sulfur contents, usually contains a range of refractory stringent organosulfur compounds and their derivatives that are difficult to eradicate through traditionally used hydrodesulfurization processes. Figure 7 indicated that the key constituents of the studied diesel oil were diphenyl sulfide and dibenzothiophene. In order to achieve a clear picture of the oxidative desulfurization process, the chemical kinetics were examined based on the attained desulfurization outcomes by simulating the results against a pseudo-first-order kinetics prototype. As shown in Figure 9, the oxidative desulfurization process for real diesel comprising diphenyl sulfide and dibenzothiophene in the presence of carboxylic acid is depicted with the reaction proceeding according to trends that are well in agreement with a pseudo-first-order kinetic model, as indicated by the fact that results for the linear regression correlation coefficient (R^2) remained adjacent to 0.9–1. The kinetic equation of this specific model could be derived as follows:

$$\ln (C_o/C_t) = -k_{app}t \tag{1}$$

where C_o is the initial organosulfur compound concentration, C_t is the instantaneous organosulfur compound concentration, k_{app} is the apparent reaction rate coefficient, and t is the reaction time. For the desulfurization of real diesel, the incidence of oxidative outcomes within the pseudo-first-order reaction kinetics with the reaction time is indicated by the graph of $-\ln(C_o/C_t)$ and that of the reaction time (t). The conforming apparent reaction rate coefficients (kapp) for the succinic acid, malonic acid, and glutaric acid were 7.92×10^{-1}, 7.11×10^{-1}, and 8.36×10^{-1} h^{-1}, respectively. The k_{app} of glutaric acid was the highest and gave a significant lead to the other carboxylic acids.
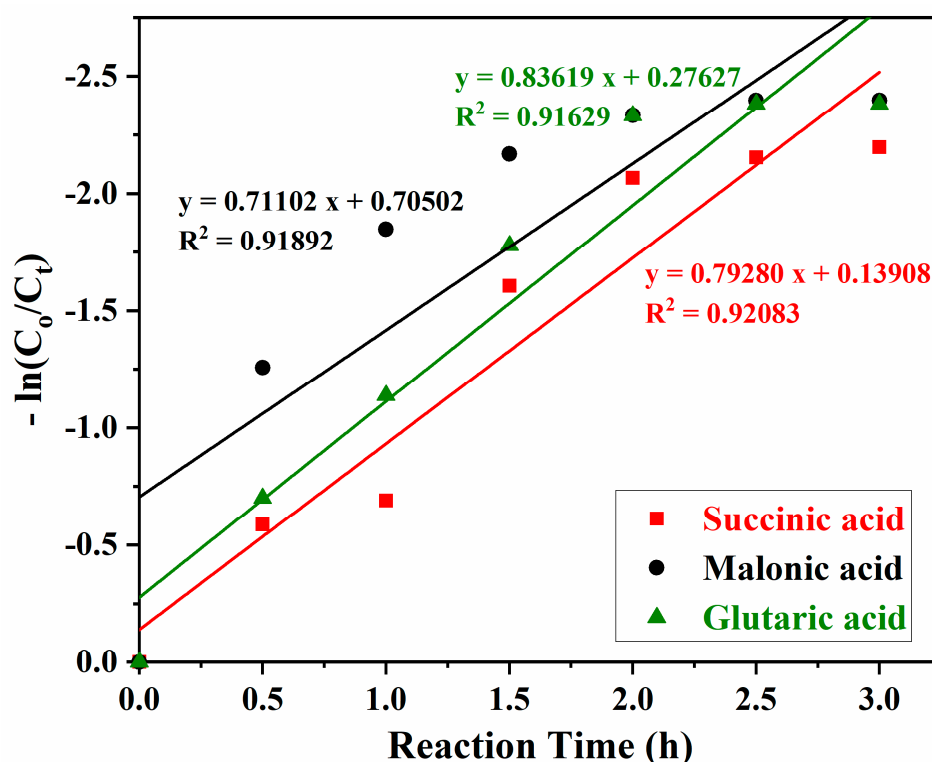

Figure 9. Kinetic study for oxidative desulfurization of real diesel.

4. Conclusions

In summary, an oxidative desulfurization system has been successfully developed and applied to remove total sulfur compounds from real untreated diesel fuel (8104 mg/L of total sulfur content). This system relied on H_2O_2 activation using three different dicarboxylic acids. The proposed oxidative–extraction coupling system has a novel, low-cost, facile,

and excellent desulfurization efficiency, making it potentially applicable in the commercial desulfurization process for untreated high-sulfur diesel fuels. The developed system has successfully removed about 92% of all sulfur compounds from the high-sulfur diesel sample (8104 mg/L). It was found that the reaction temperature, reaction time, H_2O_2 (50 $w/w\%$), and carboxylic acid dosage for optimal oxidative desulfurization are 95 °C, 6 h, 10 mL, and 0.6 g, respectively. The results suggested that the investigated dicarboxylic acids (malonic acid, succinic acid, and glutaric acid) have promising potential for the activation of H_2O_2 as an effective oxidative desulfurization system. The developed oxidative desulfurization system offers the advantages of using low-cost oxidants and mild operating conditions. The designed system has excellent desulfurization efficiency for high-sulfur diesel fuels with simple and affordable operation, giving it the potential to be applied in industrial oxidative desulfurization processes for real untreated diesel fuels.

Author Contributions: Conceptualization, B.S.A. and K.H.H.A.; methodology, B.S.A.; software, I.S.; validation, L.O.H., K.H.H.A. and K.M.O.; formal analysis, B.S.A.; investigation, B.S.A.; writing—original draft preparation, K.H.H.A.; writing—review and editing, B.S.A., L.O.H., K.M.O. and I.S.; visualization, K.H.H.A.; supervision, K.H.H.A. and L.O.H. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hai, T.; Aziz, K.H.H.; Zhou, J.; Dhahad, H.A.; Sharma, K.; Almojil, S.F.; Almohana, A.I.; Alali, A.F.; Kh, T.I.; Mehrez, S.; et al. Neural network-based optimization of hydrogen fuel production energy system with proton exchange electrolyzer supported nanomaterial. *Fuel* **2023**, *332*, 125827. [CrossRef]
2. Chandran, D.; Khalid, M.; Walvekar, R.; Mubarak, N.M.; Dharaskar, S.; Wong, W.Y.; Gupta, T.C.S.M. Deep eutectic solvents for extraction-desulphurization: A review. *J. Mol. Liq.* **2019**, *275*, 312–322. [CrossRef]
3. Mwangi, J.K.; Lee, W.-J.; Chang, Y.-C.; Chen, C.-Y.; Wang, L.-C. An overview: Energy saving and pollution reduction by using green fuel blends in diesel engines. *Appl. Energy* **2015**, *159*, 214–236. [CrossRef]
4. Fraile, J.M.; Gil, C.; Mayoral, J.A.; Muel, B.; Roldán, L.; Vispe, E.; Calderón, S.; Puente, F. Heterogeneous titanium catalysts for oxidation of dibenzothiophene in hydrocarbon solutions with hydrogen peroxide: On the road to oxidative desulfurization. *Appl. Catal. B Environ.* **2016**, *180*, 680–686. [CrossRef]
5. De Leon, J.D. Binary γ-Al2O3–α-Ga2O3 as supports of NiW catalysts for hydrocarbon sulfur removal. *Appl. Catal. B Environ.* **2016**, *181*, 524–533. [CrossRef]
6. Saleh, T.A. Carbon nanotube-incorporated alumina as a support for MoNi catalysts for the efficient hydrodesulfurization of thiophenes. *Chem. Eng. J.* **2021**, *404*, 126987. [CrossRef]
7. Shafiq, I.; Shafique, S.; Akhter, P.; Yang, W.; Hussain, M. Recent developments in alumina supported hydrodesulfurization catalysts for the production of sulfur-free refinery products: A technical review. *Catal. Rev.* **2022**, *64*, 1–86. [CrossRef]
8. Houda, S.; Lancelot, C.; Blanchard, P.; Poinel, L.; Lamonier, C. Oxidative desulfurization of heavy oils with high sulfur content: A review. *Catalysts* **2018**, *8*, 344. [CrossRef]
9. Shafiq, I.; Hussain, M.; Shafique, S.; Rashid, R.; Akhter, P.; Ahmed, A.; Jeon, J.-K.; Park, Y.-K. Oxidative desulfurization of refinery diesel pool fractions using LaVO$_4$ photocatalyst. *J. Ind. Eng. Chem.* **2021**, *98*, 283–288. [CrossRef]
10. Saha, B.; Vedachalam, S.; Dalai, A.K. Review on recent advances in adsorptive desulfurization. *Fuel Process. Technol.* **2020**, *214*, 106685. [CrossRef]
11. Dharaskar, S.A.; Wasewar, K.L.; Varma, M.N.; Shende, D.Z.; Yoo, C. Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel. *Arab. J. Chem.* **2016**, *9*, 578–587. [CrossRef]
12. Bu, J.; Loh, G.; Gwie, C.G.; Dewiyanti, S.; Tasrif, M.; Borgna, A. Desulfurization of diesel fuels by selective adsorption on activated carbons: Competitive adsorption of polycyclic aromatic sulfur heterocycles and polycyclic aromatic hydrocarbons. *Chem. Eng. J.* **2011**, *166*, 207–217. [CrossRef]
13. Seredych, M.; Bandosz, T.J. Removal of dibenzothiophenes from model diesel fuel on sulfur rich activated carbons. *Appl. Catal. B Environ.* **2011**, *106*, 133–141. [CrossRef]
14. Srivastav, A.; Srivastava, V.C. Adsorptive desulfurization by activated alumina. *J. Hazard. Mater.* **2009**, *170*, 1133–1140. [CrossRef] [PubMed]

15. Hoguet, J.-C.; Karagiannakis, G.P.; Valla, J.; Agrafiotis, C.; Konstandopoulos, A.G. Gas and liquid phase fuels desulphurization for hydrogen production via reforming processes. *Int. J. Hydrogen Energy* **2009**, *34*, 4953–4962. [CrossRef]

16. Ahmad, W.; Ahmad, I.; Ishaq, M.; Ihsan, K. Adsorptive desulfurization of kerosene and diesel oil by Zn impregnated montmorollonite clay. *Arab. J. Chem.* **2017**, *10*, S3263–S3269. [CrossRef]

17. Yu, G.; Lu, S.; Chen, H.; Zhu, Z. Diesel fuel desulfurization with hydrogen peroxide promoted by formic acid and catalyzed by activated carbon. *Carbon* **2005**, *43*, 2285–2294. [CrossRef]

18. Triantafyllidis, K.S.; Deliyanni, E.A. Desulfurization of diesel fuels: Adsorption of 4, 6-DMDBT on different origin and surface chemistry nanoporous activated carbons. *Chem. Eng. J.* **2014**, *236*, 406–414. [CrossRef]

19. Mokhtar, W.N.A.W.; Abu Bakar, W.A.W.; Ali, R.; Kadir, A.A.A. Development of bimetallic and trimetallic oxides doped on molybdenum oxide based material on oxidative desulfurization of diesel. *Arab. J. Chem.* **2018**, *11*, 1201–1208. [CrossRef]

20. Saleh, T.A. Simultaneous adsorptive desulfurization of diesel fuel over bimetallic nanoparticles loaded on activated carbon. *J. Clean. Prod.* **2018**, *172*, 2123–2132. [CrossRef]

21. Sun, L.; Zhu, Z.; Su, T.; Liao, W.; Hao, D.; Chen, Y.; Zhao, Y.; Ren, W.; Ge, H.; Lü, H. Novel acidic eutectic mixture as peroxidase mimetics for oxidative desulfurization of model diesel. *Appl. Catal. B Environ.* **2019**, *255*, 117747. [CrossRef]

22. Hao, L.; Wang, M.; Shan, W.; Deng, C.; Ren, W.; Shi, Z.; Lü, H. L-proline-based deep eutectic solvents (DESs) for deep catalytic oxidative desulfurization (ODS) of diesel. *J. Hazard. Mater.* **2017**, *339*, 216–222. [CrossRef] [PubMed]

23. Hao, L.; Su, T.; Hao, D.; Deng, C.; Ren, W.; Lü, H. Oxidative desulfurization of diesel fuel with caprolactam-based acidic deep eutectic solvents: Tailoring the reactivity of DESs by adjusting the composition. *Chin. J. Catal.* **2018**, *39*, 1552–1559. [CrossRef]

24. Li, A.; Song, H.; Meng, H.; Lu, Y.; Li, C. Ultrafast desulfurization of diesel oil with ionic liquid based PMoO catalysts and recyclable NaClO oxidant. *Chem. Eng. J.* **2020**, *380*, 122453. [CrossRef]

25. Jiang, W.; Zhu, K.; Li, H.; Zhu, L.; Hua, M.; Xiao, J.; Wang, C.; Yang, Z.; Chen, G.; Zhu, W.; et al. Synergistic Effect of Dual Brønsted Acidic Deep Eutectic Solvents for Oxidative Desulfurization of Diesel Fuel. *Chem. Eng. J.* **2020**, *394*, 124831. [CrossRef]

26. Yue, D.; Lei, J.; Zhou, L.; Du, X.; Guo, Z.; Li, J. Oxidative desulfurization of fuels at room temperature using ordered meso/macroporous H3PW12O40/SiO2 catalyst with high specific surface areas. *Arab. J. Chem.* **2020**, *13*, 2649–2658. [CrossRef]

27. Aguiar, A.; Ribeiro, S.; Silva, A.M.; Cunha-Silva, L.; de Castro, B.; Silva, A.M.; Balula, S.S. An efficient eco-sustainable oxidative desulfurization process using μ-oxo-bridged Fe (III) complex of meso-tetrakis (pentafluorophenyl) porphyrin. *Appl. Catal. A Gen.* **2014**, *478*, 267–274. [CrossRef]

28. Sampanthar, J.T.; Xiao, H.; Dou, J.; Nah, T.Y.; Rong, X.; Kwan, W.P. A novel oxidative desulfurization process to remove refractory sulfur compounds from diesel fuel. *Appl. Catal. B Environ.* **2006**, *63*, 85–93. [CrossRef]

29. Ghubayra, R.; Yahya, R.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Oxidative desulfurization of model diesel fuel catalyzed by carbon-supported heteropoly acids: Effect of carbon support. *Fuel* **2021**, *301*, 121083. [CrossRef]

30. Ghubayra, R.; Nuttall, C.; Hodgkiss, S.; Craven, M.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Oxidative desulfurization of model diesel fuel catalyzed by carbon-supported heteropoly acids. *Appl. Catal. B Environ.* **2019**, *253*, 309–316. [CrossRef]

31. Timbila, S.; Donoso, C.; Mejía, F. Oxidative Desulfurization of Diesel from the Topping Plant using 1-Butyl-3-Methylimidazolium Hydrogen Sulfate [Bmim][HSO4] as Catalyst. In *IOP Conference Series: Earth and Environmental Science*; IOP Publishing: Bristol, UK, 2021.

32. Gao, H.; Guo, C.; Xing, J.; Zhao, J.; Liu, H. Extraction and oxidative desulfurization of diesel fuel catalyzed by a Brønsted acidic ionic liquid at room temperature. *Green Chem.* **2010**, *12*, 1220–1224. [CrossRef]

33. Zhu, Z.; Lin, H.; Chi, M.; Gao, X.; Feng, Y.; Yang, K.; Lü, H. Unveiling structure-function relationships in deep eutectic solvents based biomimetic catalysis for aerobic oxidative desulfurization. *Fuel* **2022**, *308*, 122070. [CrossRef]

34. Rafiee, E.; Joshaghani, M.; Abadi, P.G.-S. Oxidative desulfurization of diesel by potato based-carbon as green support for H5PMo10V2O40: Efficient composite nanorod catalyst. *J. Saudi Chem. Soc.* **2017**, *21*, 599–609. [CrossRef]

35. Yaseen, M.; Khattak, S.; Ullah, S.; Subhan, F.; Ahmad, W.; Shakir, M.; Tong, Z. Oxidative desulfurization of model and real petroleum distillates using Cu or Ni impregnated banana peels derived activated carbon–NaClO catalyst–oxidant system. *Chem. Eng. Res. Des.* **2022**, *179*, 107–118. [CrossRef]

36. Liu, Y.-Y.; Leus, K.; Sun, Z.; Li, X.; Depauw, H.; Wang, A.; Zhang, J.; Van Der Voort, P. Catalytic oxidative desulfurization of model and real diesel over a molybdenum anchored metal-organic framework. *Microporous Mesoporous Mater.* **2019**, *277*, 245–252. [CrossRef]

37. Li, A.; Song, H.; Meng, H.; Lu, Y.; Li, C. Poly (ionic liquid) s based nano core-shell catalyst SiO$_2$@ V-PIL for efficient oxidative desulfurization of diesel. *Appl. Catal. A Gen.* **2021**, *616*, 118096. [CrossRef]

38. Kargar, H.; Ghahramaninezhad, M.; Shahrak, M.N.; Balula, S.S. An Effective Magnetic Catalyst for Oxidative Desulfurization of Model and Real Fuels: Fe$_3$O$_4$/ZIF-8/TiO$_2$. *Microporous Mesoporous Mater.* **2021**, *317*, 110992. [CrossRef]

39. Julião, D.; Mirante, F.; Ribeiro, S.O.; Gomes, A.C.; Valença, R.; Ribeiro, J.C.; Pillinger, M.; de Castro, B.; Gonçalves, I.S.; Balula, S.S. Deep oxidative desulfurization of diesel fuels using homogeneous and SBA-15-supported peroxophosphotungstate catalysts. *Fuel* **2019**, *241*, 616–624. [CrossRef]

40. Huang, P.; Liu, A.; Kang, L.; Zhu, M.; Dai, B. Heteropoly acid supported on sodium dodecyl benzene sulfonate modified layered double hydroxides as catalysts for oxidative desulfurization. *New J. Chem.* **2018**, *42*, 12830–12837. [CrossRef]

41. Du, Y.; Yang, P.; Zhou, S.; Li, J.; Du, X.; Lei, J. Direct synthesis of ordered meso/macrostructured phosphotungstic acid/SiO2 by EISA method and its catalytic performance of fuel oil. *Mater. Res. Bull.* **2018**, *97*, 42–48. [CrossRef]