ISSN: 2458-8989

Natural and Engineering Sciences

NESciences, 2022, 7(3): 284-293 doi: 10.28978/nesciences.1222495

Adsorptive Desulfurization of Crude Oil with Clinoptilolite Zeolite

Vildan Özkan *, Abdullah Özkan

Iskenderun Technical University, Faculty of Engineering and Natural Science, Iskenderun, Hatay, Turkey

Abstract

Crude oil; is a fossil fuel containing carbon, hydrogen, sulfur and many other components and is one of the world's largest and most widely used energy sources. However, in order for crude oil to be used as an energy source, it must be refined. With the use of petroleum products obtained as a result of refining, very high amounts of SOx gas are released into the atmosphere. These gases seriously harm both the environment and human health. This study aimed to reduce the amount of sulfur in crude oil and reduce its possible damages by using clinoptilolite zeolite (CZ). For this purpose, first of all, CZ; was characterized by SEM and XRF. Then, 0.1 g, 0.5 g, 1 g, 2 g and 5 g of the characterized CZ were weighed and added to the 50 mL crude oil samples separately. The mixture was mixed with a magnetic stirrer at 400 rpm for 60 and 120 minutes at room temperature before going through with an adsorptive desulfurization step. Afterwards, it was separated from the adsorbent by centrifugation and the residual sulfur amount was determined by ASTM D 1552-03 method. As a result of this study, which was carried out in an experimental laboratory environment; it has been observed that the desulfurization efficiency varies between 0.75 and 5.76 % (w/v) with the use of CZ adsorbent. Moreover; it was determined that the highest sulfur removal was obtained by using 5 g CZ.

Keywords:

Crude oil, sulphur, desulphurization, clinoptilolite zeolite

Article history:

Received 14 October 2022, Accepted 20 November 2022, Available online 23 December 2022

Introduction

Access to energy; is of critical importance for the welfare, economic development and quality of life of society. Therefore, removing the barriers to access to usable energy can only be possible by

Corresponding Author: Vildan ÖZKAN, E-mail: vildan.ozkan@iste.edu.tr

increasing the usable energy. For this reason, researchers have been increasing their studies on energy in recent years and they have been making efforts to ensure that usable energy sources do not harm the environment and human health (Kavak, 2022). Throughout history, energy systems have been based on fossil fuels (coal, oil and gas). As a result of the use of fossil fuels, carbon dioxide and other greenhouse gases are released, which is expressed as the main cause of global climate change. The high amount of carbon monoxide, which is proven to be harmful to human health and the environment, resulting from the combustion of fossil fuels; sulfur oxides, SO_2 and SO_3 (represented as SOx); nitrogen oxides, NO and NO_2 (represented as NO_x) and particles come out (Sonel, 1997). In particular, due to the harmful effects of SO_x gases released as a result of combustion, the sulfur ratio in gasoline and diesel fuels has been limited. Governments strive to reduce the concentration of petroleum products like gasoline and diesel to less than 15 ppm in conformity with current rules. The sulphur limit in gasoline and diesel in the United States (USA) is 10 and 15 ppm, respectively, while it is 10 ppm in both in the European Union (EU). In contrast, Japan started carrying out the decision in 2007 to lower the sulphur content of gasoline and diesel to 10 ppm (Eßer et al., 2004; Stanislaus et al., 2010; Baeza, 2012; Ahmed, 2016; Yeole & Parthasarthy, 2022). To reduce the number of sulphur compounds in fuels, various methods such as hydrodesulphurization (Li et al., 2018; Zhou et al., 2019), oxidative desulphurization (Vickers, 2017; Rezvani et al., 2019; Wang et. Al., 2022), and extractive desulphurization (Dharaskar et al., 2014; Yang et al., 2022; Dashtpeyma et al., 2022) are used. Hydrodesulphurisation (HDS), the earliest known desulphurization technique, offers a quick reaction time and a high desulphurization effectiveness. This method, however, necessitates difficult conditions such as high temperature and pressure (Vít et al., 2015; Kazemi-Beydokhti & Hassanpour-Souderjani, 2022). The crude oil's sulphur is oxidized by sodium bromate, potassium permanganate, carboxylic acids, and sulfonic acids in the oxidative desulfurization process (Gokel et al., 1980; Kubata & Takeuchi, 2004; Shaabani et al., 2009). Adsorptive desulphurization studies have recently gained prominence due to their potential application in the desulphurization of various materials (Salehi et al., 2020; Tuna et al., 2020; Gupta et al., 2021). In this method, the hydrocarbon's sulfur and sulfur-containing compounds adhere to the solid adsorbent surface. The method's effectiveness is proportional to the adsorbent's effectiveness (Blanco-Brieva, 2010).

Recently, researchers have been working on desulfurizing crude oil using a variety of adsorbents, including carbon nanomaterials, activated carbon, metal-organic frameworks, metal oxide nanoparticles, and zeolites (Svinterikos et al., 2019).

For example; Özkan 2022 conducted a sulphur removal study using CuONPs/MWCNTs. In his study, he investigated the adsorptive desulphurization efficiency by using CuONPs/MWCNTs in amounts ranging from 0.02 to 0.01 g. As a result of the study, in which 60 and 120 minutes of contact time were tested, an efficiency of 2.47 - 5.44 % was obtained (Özkan, 2022). Yu et al. (2015) examined the impact of surface functional groups and surface morphology on the ADS of diesel range fuel for carbon-based adsorbents such as activated carbons, carbon aerogels, and carbon nanotubes. This review also discussed the effect of nitrogen and aromatic compounds in the feed on adsorptive desulfurization. For the purpose of removing sulfur, Rajendran et al. (2020) studied boron nitride-based adsorbents. These reviews investigated at a particular type of adsorbents' adsorptive desulfurization. The current review focuses on new developments in ADS as well as ADS of various absorbent types, including carbon, mesoporous materials, metal oxide, clay, industrial waste, metal-organic framework, and zeolite-based materials. Comprehensive evaluations are also made of the adsorbent regeneration methods, adsorptive desulfurization mechanisms, kinetics, and thermodynamics. Critically covered are the impacts of operating factors such adsorbent loading, working time, initial adsorbate volume, and operating temperature on the effectiveness of adsorbents. The recent advancement of adsorptive desulfurization of genuine feedstocks is also included in this paper. Liao et al. (2015), incorporation of Ag, Cu, Ni, and Zn for the removal of thiophene increased the adsorption capacity of alumina (-Al_2O_3). Silver has the best sulfur adsorption efficiency of the four metals. Watanabe et al. (2021) looked at the behavior of mixed metal oxide TiO_2-CeO_2 adsorptively desulfurizing jet fuel with 1055 ppm sulfur. The surface active oxygen species on TiO_2-CeO_2 served as active sites and adsorbed sulfur molecules through the interaction of electron donors and acceptors. The sulfur content of jet fuel was reported to be reduced to 1 ppm using this mixed metal adsorbent. Ln (BTC)(H_2O)DMF, where Ln = Samarium [Sn], Terbium [Tb], Europium [Eu], and Yttrium [Y], and BTC = benzene-1,3,5-tricarboxylate, was the subject of research by Xiang et al. (2014). Due to the distinct electronic structure of rare earth metals (an imperfect configuration of the 4f electron shell), this form of MOF proved very successful at adsorbing sulfur compounds thanks to a combination of strong electron-metal and electron-metal interactions.

By employing clinoptilolite zeolite, this research intended to reduce the amount of sulphur in crude oil and eliminate potential harm (CZ). First, SEM and XRF were used to characterize CZ for this purpose. The described CZ was then weighed, and independent additions of 0.1 g, 0.5 g, 1 g, 2 g, and 5 g were made to the 50 mL crude oil samples. By mixing the solution at 400 rpm for 60 and 120 min at room temperature, the mixture was put through an adsorptive desulfurization process. Following centrifugation to remove it from the adsorbent, the amount of residual sulfur was measured using the ASTM D 1552-03 method.

Materıal and Methods

All of the compounds used in this study were obtained from Merck and Sigma-Aldrich and were of analytical purity. Additionally, the sample of crude oil used in our investigation came from Kirkuk, Iraq. The chemical properties of the crude oil used in our study are given in Table 1.

Table 1. Chemical properties of crude oil

Chemical properties	Crude oil	Method
API gravity value	29.43	Calculation
Water & Sediment content (% v/v)	1 %	ASTM D-4007
Salt content (% w/v)	-	ASTM D-3230
Asphaltene content (% w/v)	0.3 %	ASTM D-6560
Total sulphur content (% w/v)	3.69 %	ASTM D-2622

Characterization of Clinoptilolite Zeolite

X-ray fluorescence (XRF) analysis was used to determine the clinoptilolite-rich zeolite's elemental compositions, and the results are displayed in Table 2. When the zeolite we used in our study is classified according to its chemical composition, considering the Si/Al ratios, it is seen that it is included in the middle silicate zeolite class.

Table 2. The chemical composition of the Clinoptilolite Zeolite

	Content of Oxides (wt %)									
Sample	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**
CZ	0.7	1.5	13.6	71.7	<0.1	3.9	5.6	0.3	<0.1	2.5

The CZ's morphology is assessed using SEM. Figure 1 depicted the irregular prismatic cristobalite crystals in a pore's boundary that were clinoptilolite crystals that were authigenic and euhedral in shape.

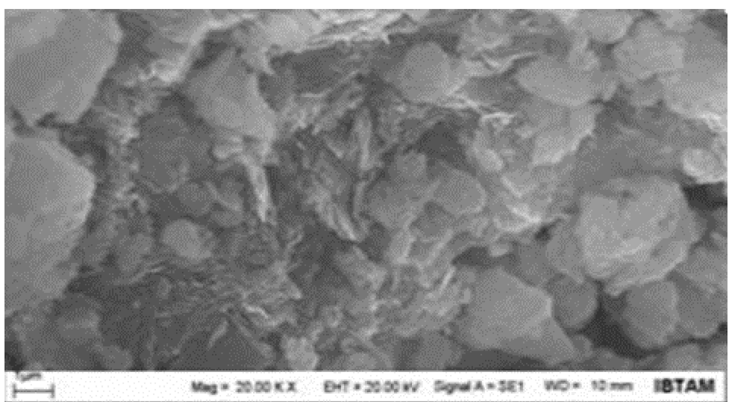

Figure 1. SEM image of CZ (Özkan & Özkan, 2019)

Sulphur Analysis

0.1 g, 0.5 g, 1 g, 2 g, and 5 g of CZ were weighed and added separately to beakers having a 100 ml capacity. After that, 50 mL of crude oil was poured into these beakers. It was stirred in a magnetic stirrer at 400 rpm for 60 and 120 minutes at room temperature to undergo an adsorptive desulfurization procedure. Each beaker's petroleum/adsorbent solution was combined, then poured into 10 ml tubes and sealed with their covers. All test tubes were prepared, and then they were centrifuged for 15 minutes at 4100 rpm to separate the crude oil from the adsorbent. After that, a disposable dropper was used to add 0.1 g of the petroleum sample that had been centrifugally separated from the adsorbent to 1 g of Com-Cat (a combustion catalyst made up of a WO_3, KH_2PO_4 mixture). Sulfur was measured after the ceramic crucible that had been created as a result of these procedures was left in the LECO 628 S device's combustion chamber. Sulfur levels were measured in accordance with the ASTM D 1552-03 standard (ASTM D1552-03 std). The technical specifications of the device used in the determination of sulphur are given in Table 3.

Table 3. The technical specifications of the device used in the determination of sulfur

Technical Specifications	Description (Values/Range)
Instrument Range	0.01 to 20 mg Sulphur
Precision (Sulphur)	0.005 mg or 1 % RSD (whicever is greater)
Nominal Sample Weight	up to 350 mg, 250 mg nominal
Detection Method	Infrared Absorption
Chemical Reagent	Magnesium Perchlorate (Anhydrous)
Gas Requirements	Oxygen, 99.5 % pure, 40 psi (2.8 bar)
Regulator Requirements	Oxygen, 0 to 125 psi (0 to 8.6 bar)
Furnace	600 to 1450 ^{o}C ±1 % of self point; Horizontal Resistance-type

Results and Discussion

As a result of this study, which was carried out with the contact time of the crude oil with the adsorbent of 60 and 120 minutes, the amount of sulfur in the crude oil was reduced at rates ranging from 0.75% to 5.76%. The desulphurization values obtained as a result of this study are given in Table 4 and Figure 2.

Table 4. Adsorbtive desulphurization and its response to various adsorbent concentrations and contact times

Sample Name		Crude Oil	1	2	3	4	5
Amount of Adsorbent (g)		-	0.1	0.5	1	2	5
Sulphur in Crude Oil (%w/v)		3.6875	3.6875	3.6875	3.6875	3.6875	3.6875
Sulphur Amount After Processing (%)	**60 min**	3.6875	3.6600	3.6440	3.6000	3.5410	3.5101
	120 min	3.6875	3.6355	3.6120	3.5550	3.5105	3.4753
Desulphurization Efficiency (%)	**60 min**	3.6875	0.7458	1.1797	2.3729	3.9729	4.8102
	120 min	3.6875	1.4102	2.0475	3.5932	4.800	5.7546

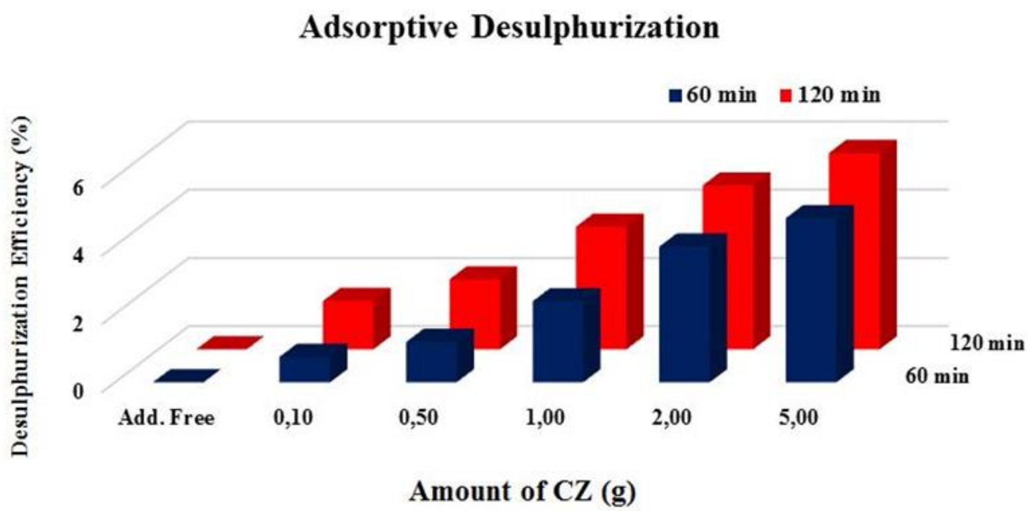

Figure 2. The impact of CZ contact time and quantity on adsorptive desulphurization

When the results obtained are examined, it is seen that the amount of sulfur adsorbed increases as the contact time of CZ with crude oil increases. Similarly, it was determined that the desulphurization efficiency increased in parallel with the increasing amount of CZ. As can be seen from the results given in Table 4, CZ can be used as an adsorbent for the removal of sulfur in crude oil. In addition, when all the results were compared among themselves, it was determined that the best result was obtained by contacting 5 g CZ adsorbent with crude oil for 120 minutes.

Similar results were observed when compared with similar studies in the literature. For example; Özkan (2022) used CuONPs/MWCNTs for the desulphurization of crude oil and stated that the desulphurization efficiency increased in parallel with the increasing amount of adsorbent and the increase in contact time. As a result of his study, he achieved sulfur removal of around 5% as a result of the contact time of 0.01 g nanomaterial for 120 minutes. Khaled similarly contrasted the ability of MWCNTs, graphene oxide, and activated carbon to remove thiophene and dibenzothiophene (DBT) from diesel fuel. In all three adsorbents employed in the investigation, it was discovered that DBT adsorbed more easily than thiophene. According to the author, this results from the two molecules' different dipole moments. He added that the success of the investigation was enhanced by the growing amount of adsorbent. Gördük et al. in their work to reduce the amount of sulfur in crude oil in 2022, they used multi-walled carbon nanotubes functionalized with aluminium oxide nanoparticles. They stated that increasing the amount of adsorbent decreased the amount of sulphur in crude oil and they achieved a success rate of 4.75% as a result of their studies.

Finally, this study, in which CZ was used as an adsorbent and aimed to remove sulfur from crude oil, was carried out in accordance with ASTM D-1552-03 standard and 5.76% sulfur removal was achieved. It has been concluded that more successful results will be obtained if modifications are made taking into account the porous structure of CZ in the following periods. Thus, the presence of sulfur compounds in crude oil will be reduced and important work will be done in order to leave a cleaner future for future generations.

Acknowledgement

We would like to thank Prof. Dr. Tolga DEPCİ for his contributions to the characterization of Clinoptilolite Zeolite.

Author Contributions

All authors read the final version of the manuscript and approved it for publication.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

Ahmed, M.J. (2016). Preparation of activated carbons from date (*Phoenix dactylifera* L.) palm stones and application for wastewater treatments. *Process Safety and Environmental Protection*, 102, 168-182. https://doi.org/10.1016/j.psep.2016.03.010.

ASTM D1552-03, Standard test method for sulfur in petroleum products (hightemperature method). *Annual Book of Standards* (American Society for Testing and Materials (ASTM), West Conshohocken, PA) Vol. 05.01 (2000).

Baeza, P., Aguila, G., Vargas, G., Ojeda, J., & Araya, P. (2012). Adsorption of thiophene and dibenzothiophene on highly dispersed Cu/ZrO_2 adsorbents. *Applied Catalysis B: Environmental*, 111, 133-140. https://doi.org/10.1016/j.apcatb.2011.09.026.

Blanco-Brieva, G., Campos-Martin, J.M., Al-Zahrani, S.M., & Fierro, J.L.G. (2010). Removal of refractory organic sulfur compounds in fossil fuels using MOF sorbents. *Global NEST Journal*, 12(3), 296-304.

Dashtpeyma, G., Shabanian, S.R., Ahmadpour, J., & Nikzad, M. (2022). The investigation of adsorption desulphurization performance using bimetallic CuCe and NiCe mesoporous Y zeolites: Modification of Y zeolite by H4EDTA-NaOH sequential treatment. *Fuel Processing Technology*, 235, 107379. https://doi.org/10.1016/j.fuproc.2022.107379.

Dharaskar, S.A., Wasewar, K.L., Varma, M.N., Shende, D.Z., Tadi, K.K., & Yoo, C.K. (2014). Synthesis, characterization, and application of novel trihexyl tetradecyl phosphonium bis (2, 4, 4-trimethylpentyl) phosphinate for extractive desulfurization of liquid fuel. *Fuel Processing Technology*, 123, 1-10. https://doi.org/10.1016/j.fuproc.2014.02.001.

Eßer, J., Wasserscheid, P., & Jess, A. (2004). Deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green Chemistry*, 6(7), 316-322. https://doi.org/10.1039/B407028C.

Gokel, G.W., Gerdes, H.M., & Dishong, D.M. (1980). Sulfur heterocycles. 3. Heterogeneous, phase-transfer, and acid-catalyzed potassium permanganate oxidation of sulfides to sulfones and a survey of their carbon-13 nuclear magnetic resonance spectra. *The Journal of Organic Chemistry*, 45(18), 3634-3639. https://doi.org/10.1021/jo01306a019.

Gupta, N.K., Bae, J., Kim, S., & Kim, K.S. (2021). Fabrication of Zn-MOF/ZnO nanocomposites for room temperature H2S removal: Adsorption, regeneration, and mechanism. *Chemosphere*, 274, 129789. https://doi.org/10.1016/j.chemosphere.2021.129789.

Kavak, Y and Haspolat, K. (2002). Farklı Yaklaşımlarla Enerji Kaynakları. Orient Yayınları, Gaziosmanpaşa– Çankaya/Ankara, Turkey.

Kazemi-Beydokhti, A., & Hassanpour-Souderjani, H. (2022). Physical and chemical surface modification of carbon nanotubes for adsorptive desulfurization of aromatic impurities in diesel fuel. *Environmental Science and Pollution Research*, 29(22), 33558-33571. https://doi.org/10.1007/s11356-022-18576-6.

Kubota, A. & Takeuchi, H. (2004). An Unexpected Incident with m-CPBA. *Organic Process Research & Development*, 8, pp. 1076-1078.

Li, Y., Chi, K., Zhang, H., Du, P., Hu, D., Xiao, C., ... & Xu, C. (2018). The influence of hydrothermal crystallization temperature on a novel FDU-12 mesoporous composite assembled by ZSM-5 nanoclusters and its hydrodesulfurization performance for DBT and FCC diesel. *Fuel Processing Technology*, 180, 56-66. https://doi.org/10.1016/j.fuproc.2018.08.010.

Liao, J., Wang, Y., Chang, L., & Bao, W. (2015). Preparation of M/γ-Al2O3 sorbents and their desulfurization performance in hydrocarbons. *RSC Advances*, 5, pp. 62763-62771. https://doi.org/10.1039/c5ra06430a.

Özkan, A. (2022). Novel Research on the Use of Multi-Wall Carbon Nanotubes Functionalized with Copper Oxide Nanoparticles in the Adsorptive Desulphurization of Crude Oil: Laboratory Research. *ECS Journal of Solid State Science and Technology*, 11(9), 091012. https://doi.org/10.1149/2162-8777/ac9337.

Özkan, A., & Özkan, V. (2019). Effect of Clinoptilolite-Rich Zeolite on the Properties of Water Based Drilling Fluid. *Fresenius Environmental Bulletin*, 28(3), 2232-2237.

Rajendran, A., Fan, H.X., Feng, J., & Li, W.Y. (2020). Desulfurization on Boron Nitride and Boron Nitride-based Materials. *Chemistry–An Asian Journal*, 15(14), 2038-2059. https://doi.org/10.1002/asia.202000479.

Rezvani, M.A., Shaterian, M., Aghbolagh, Z.S., & Akbarzadeh, F. (2019). Synthesis and characterization of new inorganic-organic hybrid nanocomposite PMo11Cu@ MgCu2O4@ CS as an efficient heterogeneous nanocatalyst for ODS of real fuel. *ChemistrySelect*, 4(20), 6370-6376. https://doi.org/10.1002/slct.201900202.

Salehi, E., Askari, M., Afshar, S., Eidi, B., & Aliee, M. H. (2020). Adsorptive desulfurization of wild naphtha using magnesium hydroxide-coated ceramic foam filters in pilot scale: Process optimization and sensitivity analysis. *Chemical Engineering and Processing-Process Intensification*, 152, 107937. https://doi.org/10.1016/j.cep.2020.107937.

Shaabani, A., Behnam, M., & Rezayan, A.H. (2009). Tungstophosphoric acid (H3PW12O40) catalyzed oxidation of organic compounds with NaBrO3. *Catalysis Communications*, 10(7), 1074-1078. https://doi.org/10.1016/j.catcom.2008.12.059

Sonel, N. (1997). Petrol Jeolojisi. AÜFF Döner Sermaye İşletmesi Yayınları, No:46, Ankara, Turkey.

Stanislaus, A., Marafi, A., & Rana, M.S. (2010). Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. *Catalysis Today*, 153(1-2), 1-68. https://doi.org/10.1016/j.cattod.2010.05.011.

Svinterikos, E., Zuburtikudis, I., Al-Marzouqi, M. (2019). Carbon Nanomaterials for the Adsorptive Desulfurization of Fuels. *Journal of Nanotechnology*, pp. 1-13, https://doi.org/10.1155/2019/2809867.

Tuna, Ö., Simsek, E.B., Sarıoğlan, A., & Çetin, Y.D. (2020). Multifunctional and highly active zinc titanate incorporated with copper for adsorptive hot syngas desulfurization and photocatalytic dye degradation. *Journal of the Taiwan Institute of Chemical Engineers*, 112, 388-396. https://doi.org/10.1016/j.jtice.2020.04.008.

Vickers, N.J. (2017). Animal communication: when i'm calling you, will you answer too?. *Current Biology*, 27(14), R713-R715. https://doi.org/10.1016/j.cub.2017.05.064

Vít, Z., Gulková, D., Kaluža, L., & Kupčík, J. (2015). Pd–Pt catalysts on mesoporous SiO2–Al2O3 with superior activity for HDS of 4, 6-dimethyldibenzothiophene: Effect of metal loading and support composition. *Applied Catalysis B: Environmental*, 179, 44-53. https://doi.org/10.1016/j.apcatb.2015.04.057.

Wang, J., Yang, B., Peng, X., Ding, Y., Yu, S., Zhang, F., ... & Guo, J. (2022). Design and preparation of polyoxometalate-based catalyst $[MIMPs]_3PMo_6W_6O_{40}$ and its application in deep oxidative desulfurization with excellent recycle performance and low molar O/S ratio. *Chemical Engineering Journal*, 429, 132446. https://doi.org/10.1016/j.cej.2021.132446.

Watanabe, S., Ma, X., & Song, C. (2021). Adsorptive desulfurization of jet fuels over TiO_2-CeO_2 mixed oxides: role of surface Ti and Ce cations. *Catalysis Today*, 371, 265-275. https://doi.org/10.1016/j.cattod.2020.07.071.

Xiang, L., Jingyan, W., Qingyuan, L., Jiang, S., Zhang, T., & Shengfu, J.I. (2014). Synthesis of rare earth metal-organic frameworks (Ln-MOFs) and their properties of adsorption desulfurization. *Journal of Rare Earths*, 32(2), 189-194. https://doi.org/10.1016/S1002-0721(14)60050-8.

Yang, N., Lu, L., Zhu, L., Wu, P., Tao, D., Li, X., ... & Zhu, W. (2022). Phosphomolybdic acid encapsulated in ZIF-8-based porous ionic liquids for reactive extraction desulfurization of fuels. Inorganic *Chemistry Frontiers*, 9(1), 165-178. https://doi.org/10.1039/D1QI01255J.

Yeole, N.R., & Parthasarthy, V. (2022). Design of experiments (DOE) for adsorptive desulfurization (ADS) of liquid fuels–A review. Materials Today: *Proceedings*, 57, 1613-1618. https://doi.org/10.1016/j.matpr.2021.12.230

Yu, M., Zhang, N., Fan, L., Zhang, C., He, X., Zheng, M., & Li, Z. (2015). Removal of organic sulfur compounds from diesel by adsorption on carbon materials. *Reviews in Chemical Engineering*, 31(1), 27-43. https://doi.org/10.1515/revce-2014-0017.

Zhou, W., Zhou, A., Zhang, Y., Zhang, C., Chen, Z., Liu, L., ... & Tao, X. (2019). Hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiMo supported on Ga-modified Y zeolites catalysts. *Journal of Catalysis*, 374, 345-359. https://doi.org/10.1016/j.jcat.2019.05.013.