

Synergistic Influence of Non-Thermal Plasma and Hydrogen Peroxide on Oxidative Desulfurization (ODS) of Model Fuel

Noor M. Abdullah ^{*1}, Hussien Q. Hussien ¹, Rana R. Jalil ²

¹Chemical Engineering, University of Baghdad, Baghdad, Iraq.

²Petroleum Research and Development Center, Baghdad, Iraq.

*Corresponding Author.

Received 29/04/2023, Revised 01/08/2023, Accepted 03/08/2023, Published Online First 20/03/2024



© 2022 The Author(s). Published by College of Science for Women, University of Baghdad.

This is an Open Access article distributed under the terms of the [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Abstract

Desulfurization is the process of removing the organic sulfur component from fuel oils. In this work, model fuel containing the sulfur compounds benzothiophene and dibenzothiophene was oxidized using plasma technique and plasma technique assisted by 30% hydrogen peroxide. Acetonitrile was used as a polar solvent in a liquid-liquid extraction stage that followed the oxidation reaction to remove the produced sulfones from the model fuel. The oxidation process was performed at operating conditions including the molar ratio of hydrogen peroxide to sulfur (5:1), temperature 50 °C, air flow rate 75 ml/min, and voltage 11000 volts. The oxidation reaction was done using a dielectric barrier discharge process for generating non-thermal plasma. The plasma technique and a combination of plasma with hydrogen peroxide together to oxidize BT and DBT. The results showed that both methods follow the pseudo-first-order reaction and that the removal efficiency is 93.78% per cent for plasma compared to the combination of plasma and hydrogen peroxide together, which reached 95.12%. Hydrogen peroxide (H₂O₂) in an aqueous solution is the most commonly used oxidant in oxidative desulfurization. However, the use of hydrogen peroxide creates organ wastewater, which must be collected and disposed of after the reaction, whereas ozone is a highly promising oxidant for oxidative desulfurization(ODS) since it does not produce wastewater and has a greater oxidation potential (2.8V) than hydrogen peroxide (1.7V). To put oxidative desulfurization with ozone into practice, establishing a more efficient desulfurization process with ozone is extremely desirable.

Keywords: Desulfurization, Hydrogen Peroxide, Oxidation, Plasma, Sulfur.

Introduction

Environmental degradation and energy supply are now major societal challenges as a result of economic advancement and population expansion. The extensive use of fuel products in various industries generates a wide range of pollutants that can be harmful to both the environment and people's health ^{1,2}.

Sulfur dioxide, a highly poisonous gas created by the burning of sulfur-containing fuels such as coal and diesel, is toxic to both humans and the environment.

When sulfur dioxide combines with moisture, acidic rain and low pH fogs are generated. Acid rain damages aquatic life, erodes buildings, and alters soil and water chemistry³, and as a result, the creation of green fuel has demonstrated significant promise for ensuring that the environment is clean and pollution-free⁴. Environmental regulations have been introduced in many countries worldwide to reduce the sulfur content in distillate fuels to ultra-low levels (10 ppm), reducing the transportation fuel machine's

harmful exhaust emissions and improving air quality. Reducing sulfur level emission to nearly zero was named the global goal for the coming five to ten years⁵. Many catalytic oxidative or adsorption techniques may be utilized to study the removal of substances that include sulfur, which is an important step in refining petroleum. These processes should be used under optimal operating circumstances⁶. The environmental danger caused by toxic gases in the atmosphere may be reduced by removing sulfur from fuel oils with high levels of sulfur. The development of an effective desulfurization process for petroleum products is important in terms of environmental pollution, economy, product quality, and strict environmental laws. Using a variety of procedures, including hydrosulfurization⁷,⁸. Oxidative desulfurization, bio-desulfurization⁹, deep eutectic solvent extraction, and adsorptive desulfurization¹⁰, desulfurization processes have been carefully studied¹¹. Among the methods researched, oxidative desulfurization procedures are regarded as one of the most promising ways for desulfurization because of properties such as ease of processing and high desulfurization effectiveness,¹².

The oxidative desulfurization system oxidizes refractory sulfur compounds in fuel feedstocks in a series of steps to produce sulfones (first to the sulfoxide, then to the sulfone). Solvent extraction is used to remove the sulfones that result from the chemical conversion of reactive oxygen species in oxidants to sulfone molecules¹³, oxidative desulfurization appears to be a viable technology because of its potential benefits. A few of these are the lack of hydrogen, the low operating temperatures, and the strong oxidation reactivity of the most refractory sulfur-containing compounds, such as dibenzothiophene, and its alkylated derivatives¹⁴. Furthermore, because of their high polarity, oxidized sulfur-containing substances like sulfones and sulfoxides can be easily removed using liquid-liquid extraction or selective adsorption.

Hydrogen peroxide is employed as the oxidizing agent in the oxidative desulfurization process because it is economical, environmentally friendly, mildly corrosive, and commercially accessible. Yet, in the absence of a catalyst, H₂O₂ seems to be a weak oxidizing agent. Organic acids, polyoxometalate acids¹⁵, and their salts in aqueous solution have all been reported to be used as catalysts in the oxidation of organosulfur compounds to their corresponding sulfones by H₂O₂¹⁶.

Because of the significant attraction of sulfur for the electrophilic addition of oxygen, OSCs can be efficiently oxidized in the oxidative desulfurization method to produce sulfones (1-oxides) and/or sulfoxides (1, 1-dioxide) without damaging the C-C bond. In comparison to hydrocarbons, which may be easily removed by adsorption, solvent extraction, or distillation, oxidized sulfur compounds are considerably more polar. In comparison to other oxidation systems, hydrogen peroxide (H₂O₂) is favored because of its strong oxidation capacity, cheapness, and production of water byproducts that are favorable to the environment. But still, the creation of a biphasic system when employing H₂O₂ in fuel oil is a crucial factor to take into account. To further enhance desulfurization performance, this has to be handled¹⁷.

The rate of sulfur oxidation declined in the following order: 4,6-DMDBT > 4-MDBT > DBT > BT, and thiophene compounds with electron densities of 5.696 to 5.716 on the sulfur atoms were unable to be oxidized at 50°C. It is possible to oxidize BT, which has a 5.739 electron density, as well as other benzothiophene and dibenzothiophene molecules.

Organic sulfides in the liquid phase are desulfurized by plasma oxidation. Plasma oxidative desulfurization has a high rate of reaction activation and can prevent the poisoning of catalysts. Thiophene normally cannot be easily oxidized due to the strength of the C-S bond; however, when plasma and active oxygen are present, thiophene may be rapidly removed, generating a variety of solid sulfides that can be easily separated. The rate of thiophene desulfurization can approach 80%. To get beyond the limitations of raw materials like hydrogen while also getting a greater desulfurization result, liquid plasma oxidative desulfurization is an efficient method.

Hameed et.al.¹⁸ investigated the catalytic activity of Fe₂O₃ supported on Graphene for the oxidation desulfurization (ODS) by hydrogen peroxide (H₂O₂) of Iraqi gas oil with a sulfur concentration of 9400 ppm. The greatest sulfur removal efficiency of 90% was found at stirring times of 240 minutes, 1.5 g, and 60 °C, respectively. The catalyst activity was examined within a temperature range of 40 to 60 °C, stirring times of 160 to 240 minutes, and catalyst dosages of 0.5 to 2.5 g. Additionally, a pseudo-first-order reaction with a reaction rate governs the ODS reaction.

Jalil et.al.¹⁹ prepared **NiO** - CoO bimetallic catalysts with two Ni/Co ratios (70:30 and 80: 20) for oxidation desulfurization .The ideal conditions include the following: catalysts at 3%, 2 grams of Na₂ CO₃, 3 hours of reflux at 400 C, 700 rpm stirrer speed, and the following volume ratio of gas oil: H₂O₂: acetic acid is extracted three times with acetonitrile at a 1:1 ratio from gas oil. The best catalyst's effectiveness allows for a maximum sulfur removal of 68.97%.

Materials and Methods

Chemicals

Benzothiophene ((97%) and Dibenzothiophene (99%) from (mackline, China), n-hexane (96%) from (Merck, Germany), and acetonitrile (ACN) (99.7%) from (hipersolve BDH England , H₂O₂ from (fluka).

2.2 Model fuel

Model Fuel was prepared by dissolving BT, and DBT in pure hexane to maintain total sulfur content of 500ppm 50% of each BT and DBT

Dielectric Barrier Discharge Reactor

The experimental setup for the ODS technique is schematically depicted in Fig.1 the device consists of a mass flow controller, an ODS reactor, and a plasma generator (11Kv). A copper rod with a diameter of 2 cm was put within the wire-cylinder reactor's quartz body, which had a 0.1 cm-thick wall and an inner diameter of 3 cm. Copper wire mesh Type 304 covered the outside. Both the high voltage (HV) and low voltage (LV) electrodes were applied to the copper rod and copper wire, respectively, with a distance of 1 cm between the two electrodes. A specific flow rate of air that was regulated by a mass flow controller was used in the DBD reactor. Plasma was created when the voltage between two electrodes was greater than the air's breakdown potential. It could quickly and continuously produce new ozone, oxygen, oxygen dioxide, and other gases.

The goal of the present study is to create an effective method for the oxidative desulfurization of model fuel. ODS of the sulfur component in simulated fuel was carried out using plasma-generated ozone alone first, and later with ozone in addition to H₂O₂ as an oxidation system. Following the oxidation stage, the model fuel performed liquid-liquid extraction using acetonitrile to remove the oxidized sulfur components.

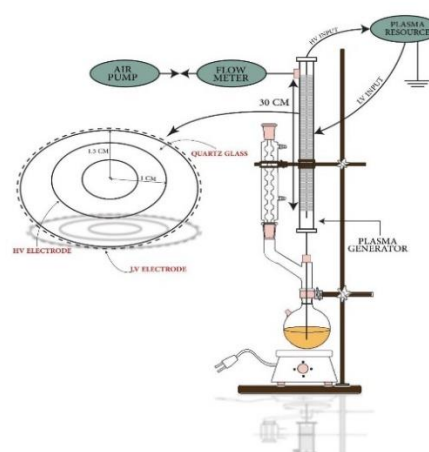


Figure 1. Dielectric barrier reactor

Method

The oxidation procedure desulfurization tests were carried out in 250 mL two-necked flasks fitted with a condenser. DBD plasma generates fresh ozone by utilizing air as a feed gas. Ozone was pumped into a flask containing 50ml of model fuel under the effect of a magnetic stirrer. After confirming oxidation at varied times (2,4,6, and 8) hours, 1:1 acetonitrile was added to extract the oxidative products BTO and/or BTO₂. The combination of oxidation product and extraction solvent was held at room temperature for 30 minutes while being constantly stirred. After 24 hours, the oil phase was separated from the water phase by employing a separating funnel. The total sulfur content of the treated samples was measured using an ICP-OES.

Furthermore, the above method was repeated, but with the addition of hydrogen peroxide (purity 30%) to the model fuel by ratio O/S (1:5) .Concurrently with plasma oxidation to enhance the oxidation efficiency.

Results and Discussion

Effects of Time on Sulfur Removal

Fig. 2 Shows how the reaction time affects sulfur conversion, assuming constant working conditions (50 °C, 75 ml/min airflow, and 11000 volts). By increasing the reaction time up to 4 hours, which was the amount of time required to complete the reactions between the model fuel and the ozone produced from DBD plasma, the sulfur removal efficiency increased. However, a further increase in response time from 4 hours to 8 hours has an equilibrium impact on the sulfur removal trend.

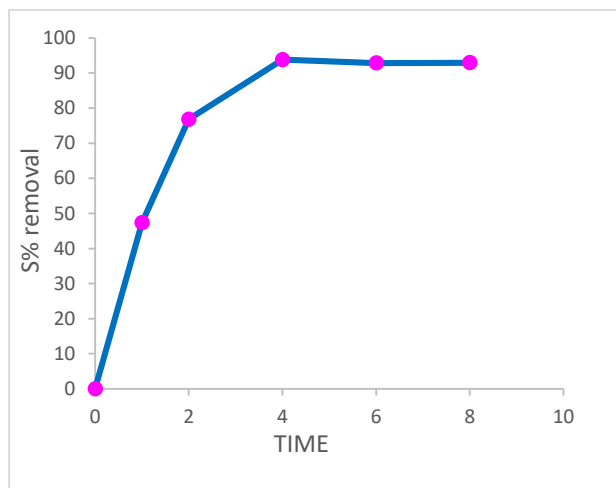


Figure 2. Sulfur removal (%) versus reaction time at 50 °C, 75 ml/min, and 11000 volts.

The Mechanism of Desulfurization is shown in Fig. 3 Ionic routes and radical reactions are two potential mechanism types for plasma reactions. Organic plasma reactions should primarily include radical reactions. To put it another way, the intense electron impact caused by the organic molecule first creates a range of active radicals, and then those radicals interact to create more stable products. Thiophene and its derivatives (BT and DBT) no longer have the weakest C-S bond, making oxidative desulfurization difficult. A nonequilibrium oxygen plasma can begin the oxidative desulfurization of BT and DBT due to its high activity and capacity to induce the thiophene ring to split apart under the impact of energetic electrons²⁰.

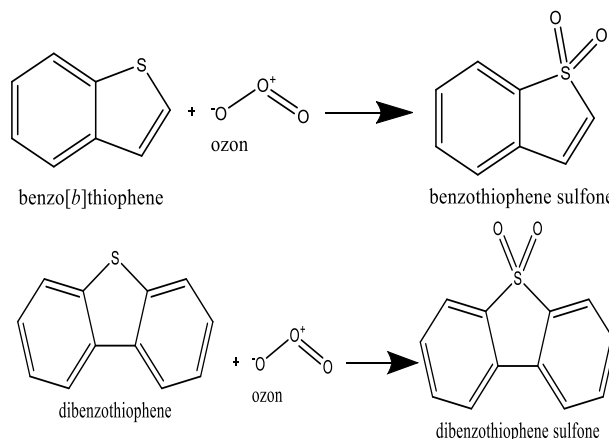


Figure 3. A scheme proposed a reaction pathway for the oxidation by plasma only of DBT and BT

Fig. 4 shows the removal of sulfur as a function of reaction time under the same working conditions (50 oC, 75 ml/min, and 11000 volts) with the addition of hydrogen peroxide as an oxidant agent with ozone. As seen in the figure, the results were improved by initially raising and then gradually reducing the reaction time. This might be explained by showing how oxidizing agents interact over time. Sulfones can be produced when H₂O₂ reacts with model fuel. This reaction, like any other, requires time to be done and grows stronger as time goes on. At 4 hours and H₂O₂/ S (5:1), the maximum efficiency was found to be 95.12%. After a certain reaction time, sulfur removal does not increase with increasing reaction time, indicating that the oxidation system has an optimal period. Although it can be observed that after the optimal value, the sulfur removal value enters equilibrium as time passes. In other words, the long reaction time and the small number of oxidizing agents both cause the absence of any oxidizing agents, a change in equilibrium, and a change in the reaction medium from oxidizing to reducing. However, when there is an excess of the primary oxidizing component of the solution (hydrogen peroxide), this tendency cannot be observed. Since the reaction media continues to be an oxidizing medium in such a situation, there are excessive numbers of hydroxyl radicals present during the whole reaction period. As a result, extending the reaction, especially when there is only a small amount of the oxidizing agent present., may not be beneficial.

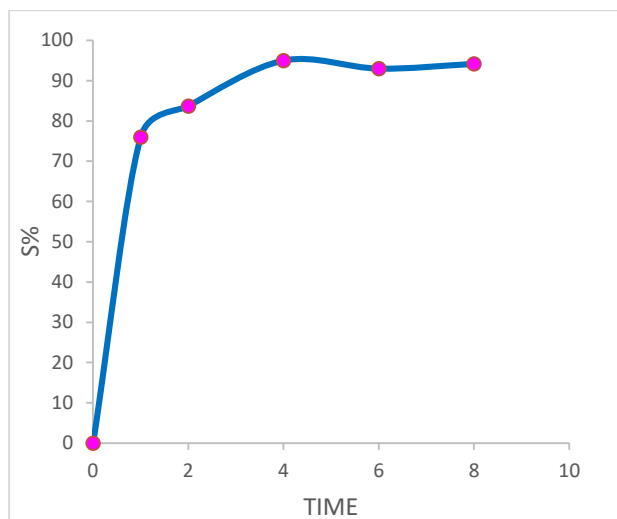


Figure 4. Sulfur removal (%) versus reaction time at 50 °C, 75 ml/min, and 11000 volts, O/S (1:5).

Fig. 5 shows the typical multistep mechanism that was used for the current reactions, the sulfur atoms in organic sulfur compounds can be attacked by the generated H_2O_2 and oxidized.

As demonstrated below, the oxidation process yields sulfones in two steps and DBT sulfoxide ($\text{C}_{12}\text{H}_8\text{S}$) molecules in one step. Because of their strong polarity, these oxidized sulfur compounds are easily recovered from diesel using solvent extraction procedures²¹.

By attacking BT with radicals, the oxidation route creates the appropriate sulfone. Ozone breaks down hydrogen peroxide to produce hydroxyl radicals ($\bullet\text{OH}$). As hydroxyl radicals are extremely potent oxidants and the oxidation electrode potential may reach 2.80 V, BT can be effectively oxidized using this method. On the other hand, a competitive pathway that involves the breakdown of hydrogen peroxide to oxygen and water as illustrated in pathway 2 hindered and controlled the oxidative activity of hydrogen peroxide in the CatODS process. That is to say, not all of the hydrogen peroxide required to oxidize BT was formed in situ as hydroxyl radicals^{22, 23}.

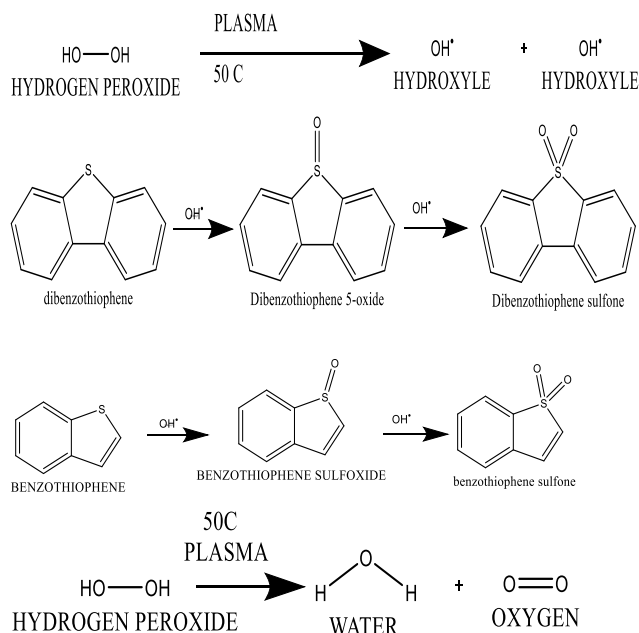


Figure 5. A scheme Proposed reaction pathway for the oxidation by plasma and H_2O_2 of DBT and BT

Desulfurization Comparisons at Different Desulfurization Systems:

In the oxidation desulfurization process, (BT, DBT) has been chosen as the typical sulfur component in fuels. Therefore, the following ODS tests were studied using model fuel that contains (BT and DBT) and has a sulfur concentration of 500 ppm. To evaluate the different oxidant activities on desulfurization systems, H_2O_2 and a combination of H_2O_2 and O_3 generated from plasma were selected as oxidants, and the reaction time was 60 min to investigate the best desulfurization systems. Furthermore, the result was compared between H_2O_2 or a combination of H_2O_2 and plasma. The results are shown in Fig. 6 from the figure it can be seen that the model fuel with a sulfur content of 500 ppm was removed when H_2O_2 , plasma, and H_2O_2 were used respectively as oxidants. However, sulfur removal was only 45.67% and 76.85 respectively under the same experimental conditions. This result showed that the oxidizing ability of plasma and H_2O_2 on sulfur content was investigated with the best result compared with another oxidant system. However, it is difficult to distribute a little amount of H_2O_2 in oil because of their immiscibility and high interfacial tension, and commercial reactors are ineffective for such a heterogeneous ODS process. Three techniques can be utilized to induce heterogeneous oxidation, namely, (1) by adding an emulsifier in

order to generate an emulsified layer, a pseudo homogenous reaction region is formed, (2) by putting catalysts at the oil/water interface that resembles surfactants, and (3) by adding an extractant into the mixture to generate an ECODS process. These methods led to several problems., such as oil emulsion, extractant contaminants, and greater separation cost²⁴. While ozone combined with hydrogen peroxide was used as an advanced oxidation process for removing (BT, and DBT) from model oil. BT and DBT were readily oxidized by ozone and hydroxyl radicals produced by ozone and hydrogen peroxide.

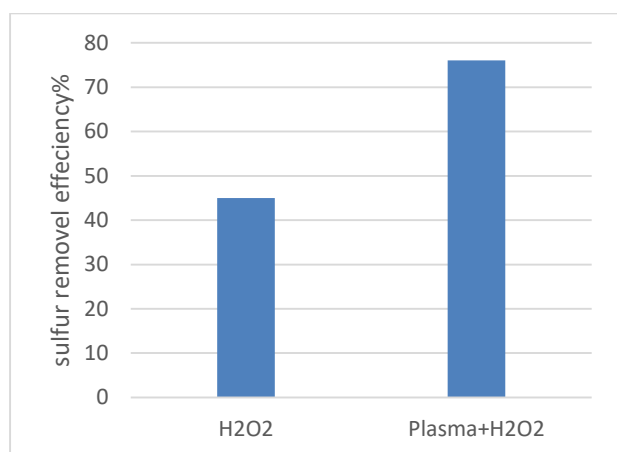


Figure 6. Effect of oxidant system on oxidation desulfurization

Kinetics of Oxidation

Kinetic modeling is one way for studying response behavior. Zero, pseudo-first, and pseudo-second-order kinetic models are the most commonly utilized²⁵.

The oxidation kinetics can be calculated by measuring the sulfur content before and after oxidation as a function of time. The determination of the kinetic model for the oxidation of sulfur compounds is done in the following Eq. 1:

$$-\frac{d[C_{sulfur}]}{dt} = K[C_{oxidant\ agent}]^a[C_S]^b \quad \dots 1$$

Where [Oxidant agent] and [C Sulfur] denote the concentrations of oxidant agents (O3 or OH.) and sulfur compounds (BT and DBT) exposed for oxidation reaction, respectively; a and b represent the order of reaction to the concentrations of oxidant agents and sulfur compounds, respectively, Pseudo-first order reaction kinetics governs how aromatic

sulfur compounds oxidize. The concentration of the oxidant agent was thought to stay constant during the process. Therefore, Eq. 2 is reduced as follows²⁶.

$$-\frac{d[C_{sulfur}]}{dt} = K'[C_S]^b \quad \dots 2$$

The pseudo-first-order catalytic oxidation reaction's linearized version for BT or DBT is shown in Eq. 3

$$\ln \frac{[C_0]}{[C_t]} = K't \quad \dots 3$$

Where [Co] and [Ct] stand for the model sulfur compound concentrations (ppm) at time 0 min and a specific time t min, respectively, and k's stands for the reaction's oxidation kinetic rate constant²⁷.

The plot of Eq. 3 Vs reaction time (t) showed a linear relationship, confirming the goodness of fit of the pseudo-first-order reaction kinetics for plasma and plasma mixed with hydrogen peroxide. 0.6992 and 0.7833 min⁻¹, respectively, are the kinetic rate constants. This explains how, when plasma and H₂O₂ were used in conjunction, a large proportion of sulfur was converted in a short period. The faster the reaction is because of a high-rate constant value^{28,29}

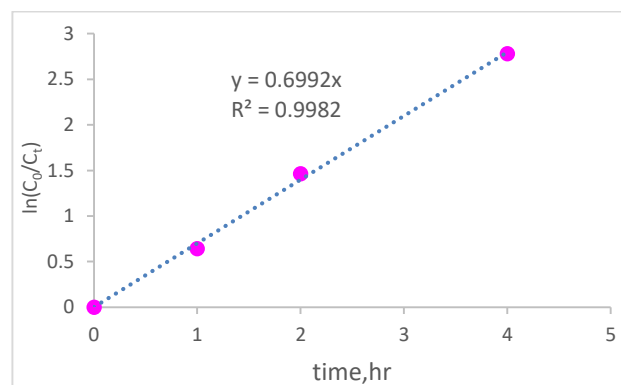


Figure 7. Oxidation kinetics of plasma oxidation

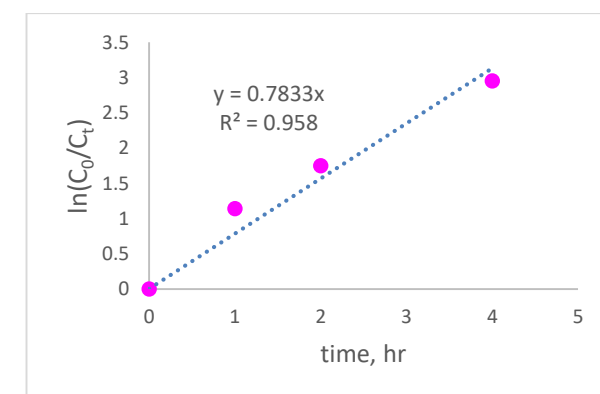


Figure 8. Oxidation kinetics of a combination of plasma and H₂O₂.

Conclusion

In this study, oxidation desulfurization for model fuel was investigated in two steps oxidation: extraction step followed by step by acetonitrile, at operating condition (11Kv, 75 ml/min, 50°C) the oxidation reaction was done using the plasma technique and a combination of plasma with hydrogen peroxide together to oxidize BT and DBT. The results showed that both methods follow the pseudo-first-order reaction and that the removal efficiency is 93.78% per cent for plasma compared to the combination of plasma and hydrogen peroxide together, which reached 95.12%. This difference in efficiency is not

considered effective in terms of economic aspects (consumption of chemicals), as it is possible to suffice with the plasma technique. Hydrogen peroxide oxidant reagent creates organic wastewater, which must be collected and disposed of after the reaction, whereas ozone is a highly promising oxidant for oxidative desulfurization (ODS) and has a greater oxidation potential (2.8V) than hydrogen peroxide (1.7V). To put oxidative desulfurization with ozone into practice, establishing a more efficient desulfurization process with ozone is extremely desirable.

Acknowledgment

This research was financially and technically supported by the Petroleum Research and Development Centre/Iraqi Oil ministry.

Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been

- included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' Contribution Statement

N. M. A. performed design, acquisition of data, analysis, interpretation, drafting the MS. H. Q. H.

performed conception, revision and proofreading. R. R. J made the revision and proofreading.

References

1. Hai T, Hikmat Hama Aziz K, Zhou J, Dhahad HA, Sharma K, Fahad Almojil S. Neural network based optimization of hydrogen fuel production energy system with proton exchange electrolyzer supported nanomaterial. *Fuel*. 2023; 332: 125827. <https://doi.org/10.1016/j.fuel.2022.125827>.
2. Halim A, Mohammed AK, Hussein HK, Naife TM. Comparative Study of New Re-Ni-Mo/Al₂O₃ and Conventional Hydrodesulfurization Catalyst. *Iraqi J Chem Pet Eng*. 2015;16(4):1–9. <https://doi.org/10.31699/IJCPE.2015.4.1>.
3. Chandran D, Khalid M, Walvekar R, Mubarak NM, Dharaskar S, Wong WY. Deep eutectic solvents for extraction-desulphurization: A review. *J Mol Liq*. 2019; 275: 312–322. <https://doi.org/10.1016/J.MOLLIQ.2018.11.051>.
4. Wang F, Harindintwali JD, Yuan Z, Wang M, Wang F, Li S, et al. Technologies and perspectives for achieving carbon neutrality. *The Innovation*. 2021;2(4): 100180. <https://doi.org/10.1016/J.XINN.2021.100180>.
5. Yahya MM, Hussein HQ. Adsorption Desulfurization Of Iraqi Heavy Naphtha Using Zeolite 13x. *JAARU*. 2019; 26(2): 12–18. <https://doi.org/10.33261/jaaru.2019.26.2.003>.
6. Kaluža L, Palcheva R, Jiráková K, Tyuliev G, Gulková D, Dimitrov L, et al. Characterization and HDS activity of Mo and NiMo sulfide catalyst prepared by thioglycolic acid assisted hydro thermal deposition method. *J Alloys Compd*. 2022; 903: 163925. <https://doi.org/10.1016/j.jallcom.2022.163925>.
7. Abdul-Halim AK, Abdul-Monaem AK, Hiadar AA. Kinetic Studies of Hydrodesulfurization of Vacuum Distillate. *Iraqi J Chem Pet Eng*. 2009; 10(1): 53–57. <https://doi.org/10.31699/IJCPE.2009.1.8>.
8. Ahmed DJ, Al-Abdaly BI, Hussein SJ. Synthesis and Characterization of New nano catalyst Mo-Ni /TiO₂-γAl₂O₃ for Hydro desulphurization of Iraqi Gas Oil.

- Baghdad Sci J. 2021; 18(4): 1557–1567. [https://doi.org/10.21123/bsj.2021.18.4\(Suppl.\).1557](https://doi.org/10.21123/bsj.2021.18.4(Suppl.).1557).
9. Alyassiry AA, Alrubaye RTA. Desulfurization of model gasoline using metal-organic frame-work. AIP Conf Proc. 2020; 2213(1): 020090. <https://doi.org/10.1063/5.0000242>.
10. Mousa HJ, Hussein HQ. Adsorptive Desulfurization of Iraqi Heavy Naphtha Using Different Metals over Nano Y Zeolite on Carbon Nanotube. Iraqi J Chem Pet Eng. 2020; 21(1): 23–31. <https://doi.org/10.31699/ijcpe.2020.1.4>.
11. Saleh TA. Characterization, determination and elimination technologies for sulfur from petroleum: Toward cleaner fuel and a safe environment. Trends Environ Anal Chem. 2020; 25: e00080. <https://doi.org/10.1016/j.teac.2020.e00080>.
12. Ahmed GS, Humadi JI, Aabid AA. Mathematical Model, Simulation and Scale up of Batch Reactor Used in Oxidative Desulfurization of Kerosene. Iraqi J Chem Pet Eng. 2021; 22(3): 11–17. <https://doi.org/10.31699/ijcpe.2021.3.2>.
13. Dalya J, Basim I, Sattar J. Synthesis and Characterization of New nano catalyst Mo-Ni /TiO₂- γ Al₂O₃ for Hydrodesulphurization of Iraqi Gas Oil. Baghdad Sci. J. 2021, 18(4): 1557-1567. [https://dx.doi.org/10.21123/bsj.2021.18.4\(Suppl.\).1557](https://dx.doi.org/10.21123/bsj.2021.18.4(Suppl.).1557).
14. Hossain MN, Park HC, Choi HS. A Comprehensive Review on Catalytic Oxidative Desulfurization of Liquid Fuel Oil. Catalysts. 2019; 9(3): 229. <https://doi.org/10.3390/CATAL9030229>.
15. Mundher Y, Hussein HQ, Al-Tabbakh BA. Synthesis and Characterization of (TBAPW11O39) Hybrid Keggin Type Catalyst. AIP Conf Proc. 2022; 2660(1): 020092 <https://doi.org/10.1063/5.0107720>.
16. Ahmed BS, Hamasalih LO, Hama Aziz KH, Omer KM, Shafiq I. Oxidative Desulfurization of Real High-Sulfur Diesel Using Dicarboxylic Acid/H₂O₂ System. Processes. 2022; 10(11): 2327. <https://doi.org/10.3390/PR10112327>.
17. Ban A, Mustafa H, Ali I, Waleed I. A Competitive Study Using UV and Ozone with H₂O₂ in Treatment of Oily Wastewater. Baghdad Sci J. 2020, 17(4): 1177-1182. <http://dx.doi.org/10.21123/bsj.2020.17.4.1177>
18. Alwan HH, Ali AA, Makki HF. Optimization of oxidative desulfurization reaction with Fe₂O₃ catalyst supported on graphene using box-behnken experimental method. Bull Chem React. 2020; 15(1): 175–185. <https://doi.org/10.9767/BCREC.15.1.6670.175-185>
19. Ugal JR, Hussein AH. Preparation and Characterization of Bimetallic Catalyst (NiO – CoO) for Desulfurization of Gas Oil. Baghdad Sci J. 2016; 13(2s(Supplement)): 0075–0075. The 2nd National Conference of Chemistry. <https://doi.org/10.21123/BSJ.2016.13.2.2NCC.0075>
20. Liu WY, Lei ZL, Wang JK. Kinetics and mechanism of plasma oxidative desulfurization in liquid phase. Energy Fuels, 2001; 15(1): 38–43. <https://doi.org/10.1021/ef000039p>
21. Abdullah GH, Xing Y. Oxidation of Dibenzothiophene in Diesel with in Situ Produced Hydrogen Peroxide. Energy Fuels. 2018; 32(8): 8254–8258. <https://doi.org/10.1021/acs.energyfuels.8b01630>
22. Wang GJ, Zhang JK, Liu Y. Catalytic oxidative desulfurization of benzothiophene with hydrogen peroxide over Fe/AC in a biphasic model diesel-acetonitrile system. Korean J Chem Eng. 2013; 30(8): 1559–1565. <https://doi.org/10.1007/S11814-013-0052-5>.
23. Chen Y, Tian Q, Tian Y, Cui J, Wang G. Ultra-Deep Oxidative Desulfurization of Fuel with H₂O₂ Catalyzed by Mesoporous Silica-Supported Molybdenum Oxide Modified by Ce. Appl Sci. 2021; 11(5): 2018. <https://doi.org/10.3390/app11052018>.
24. Li L, Lu Y, Meng H, Li C. Lipophilicity of amphiphilic phosphotungstates matters in catalytic oxidative desulfurization of oil by H₂O₂. Fuel. 2019; 253: 802–810. <https://doi.org/10.1016/j.fuel.2019.05.082>.
25. Kayedi N, Samimi A, Asgari Bajgirani M, Bozorgian A. Enhanced oxidative desulfurization of model fuel: A comprehensive experimental study. S Afr J Chem Eng. 2021; 35: 153–158. <https://doi.org/10.1016/J.SAJCE.2020.09.001>.
26. Choi AES, Roces S, Dugos N, Wan MW. Oxidation by H₂O₂ of benzothiophene and dibenzothiophene over different polyoxometalate catalysts in the frame of ultrasound and mixing assisted oxidative desulfurization. FUEL. 2016; 180: 127–136. <https://doi.org/10.1016/J.FUEL.2016.04.014>
27. Alwan HH. Oxidative desulfurization of a model fuel using MoO₃ nanoparticles supported on carbon nanotubes catalyst: Examine most significance variables, optimization, kinetics and thermodynamics study. S Afr J Chem Eng. 2022; 40: 230–239. <https://doi.org/10.1016/j.sajce.2022.03.002>
28. Lu MC, Biel LCC, Wan MW, De Leon R, Arco S. The Oxidative Desulfurization of Fuels with a Transition Metal Catalyst: A Comparative Assessment of Different Mixing Techniques. Int J Green Energy. 2014; 11(8): 833–848. <https://doi.org/10.1080/15435075.2013.830260>
29. Akopyan A V., Shlenova AO, Polikarpova PD, Vutolkina A V. High-Performance Heterogeneous Oxidative Desulfurization Catalyst with Bronsted Acid Sites. Pet Chem. 2022; 62(6): 636–642. <https://doi.org/10.1134/S0965544122040053>

المقارنة بين الأكسدة بتقنية البلازما الباردة والدمج بين تقنية البلازما مع بيروكسيد الهيدروجين للمركبات الكبريتية العضوية

نور محمد عبد الله¹، حسين قاسم حسين¹، رنا رسول جليل²

¹قسم الكيمياء، كلية الهندسة، جامعة بغداد، بغداد، العراق.
²مركز البحث والتطوير النفطي، بغداد، العراق.

الخلاصة

تتضمن إزالة الكبريت إزالة مركبات الكبريت العضوية من زيوت الوقود. في هذه الدراسة، تم استخدام تقنية البلازما الحرارية وتقنية البلازما بمساعدة بيروكسيد الهيدروجين لأكسدة الوقود المحتوي على مركبات من benzothiophene و dibenzothiophene.

تم إجراء تفاعل الأكسدة باستخدام منظومة dielectric barrier discharge لتوليد بلازما غير حرارية. النتائج أظهرت أن تقنية البلازما ومزيج من البلازما مع بيروكسيد الهيدروجين معاً لأكسدة BT و DBT. تتبعان pseudo-first-order reaction وأن كفاءة الإزالة للبلازما 93.78% مقارنة مع مزيج البلازما وبيروكسيد الهيدروجين معاً والتي بلغت 95.12%. هذا الاختلاف في الكفاءة لا يشكل فارقاً إذا ما أخذ بنظر الاعتبار الناحية الاقتصادية (استهلاك المواد الكيميائية)، حيث يمكن الاكتفاء بتقنية البلازما.

الكلمات المفتاحية: نزع الكبريت، بيروكسيد الهيدروجين، الأكسدة، البلازما، الكبريت.