Oxidative Desulfurization of Model Fuel by Non-Thermal Plasma Technology

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Abstract

   The Non-thermal plasma has a wide range of applications in different areas. In this study, the oxidation of a model fuel containing organo-sulfur compounds (benzothiophene and dibenzothiophene) was investigated using plasma. The process involved ozone generation through dielectric barrier discharge, followed by extraction using acetonitrile. The results demonstrated the efficient oxidation and removal of dibenzothiophene and benzothiophene by non-thermal plasma. The desulfurization efficiency reached 93.78% under the optimum conditions, including a voltage of 11Kv, temperature of 50ºC, duration of 4 hours, and a flow rate of 75 ml/min.

Keywords: oxidation, desulfurization, plasma, fuel, non-thermal

إزالة الكبريت بالأكسدة من الوقود النموذجي بواسطة تقنية البلازما الباردة

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الخلاصة

   البلازما غير الحرارية لها مجموعة واسعة من التطبيقات في مجالات مختلفة. في هذه الدراسة ، تمت دراسة   أكسدة الوقود النموذجي المحتوي   على مركبات عضوية– كبريتية benzothiophene و (dibenzothiophene باستخدام البلازما.. تضمنت هذه الطريقة توليد الأوزون من تباين الهواء بوساطة البلازما المتولدة من التفريغ الكهربائي عالي الفولتية ، متبوعًا بخطوة الاستخلاص باستخدام acetonitrile. أظهرت النتائج كفاءة الأكسدة وإزالة benzothiophene) و (dibenzothiophene بواسطة البلازما غير الحرارية. ، حيث كانت كفاءة الاستخلاص93.78%   عند الظروف المثلى التي تم تحديدها من خلال التجارب العملية (الفولتية 11كيلوفولط، 75مل بالدقيقة، 50درجة مئوية لمدة 4ساعات

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1. Introduction

Petroleum considers as the primary global energy source and consists of a complex mixture of hydrocarbon compounds. However, sulfur compounds present in fuel oil, such as thiophene, benzothiophene (BT), and dibenzothiophene (DBT), contribute to the release of sulfur oxides (SO) during combustion. These emissions contribute to acid rain and hinder catalyst activation during the desulfurization process in the refining industry [1-3]. To address the growing issue of air pollution, governments worldwide are implementing stricter regulations to limit sulfur concentrations in fuel sources and reduce SO emissions [4-5]. According to the United States Environmental Protection Agency (USEPA) standards, reducing such sulfur-containing compounds is useful for forming clean fuel oils and accepting the new sulfur content standards (between 10 and 15 ppm). Because sulfur creates environmental risks [6-7]. Various desulfurization methods are shown in the literature, including alkylation to change the boiling point of fractions, adsorption, absorption, extraction, catalytic oxidation, oxidative desulfurization, desulfurizati-hydroon and bio-desulfurization [8-9]. Among these hydrogenation techniques, the oxidation desulfurization process has garnered significant interest due to its favourable operating conditions (low pressure and temperature) and its ability to oxidize aromatic sulfur compounds. Moreover, it offers the advantage of not requiring expensive hydrogen [10-11]. The oxidative desulfurization of fuel oil involves a two-step process. In the first step, the sulfur is oxidized to its respective sulfones or sulfoxides by oxidizing agents such as O_2, O_3, H_2O_2, sulfuric acid, nitric acid and tertbutyl hydroperoxide. The second stage is the liquid-liquid extraction technique for the oxidized sulfur compounds by using an extracting agent such as dimethylformamide (DMF) and acetonitrile (ACN)[12]. Dielectric barrier discharge (DBD) is a gas discharge method commonly employed for wastewater treatment, industrial emission control, surface modification, and ozone production from oxygen or air [13]. The DBD system offers several advantages, including operation at atmospheric pressure, absence of vacuum requirements, and flexibility in electrode configurations with different geometrical shapes and gap sizes [14-16]. This non-thermal plasma technique generates a significant amount of ozone (O3), free radicals (•OH, •H, •HO2), and active oxygen (•O) when air or oxygen is used as the flowing gas [17]. Ozone, known for its high effectiveness as an oxidant, can be utilized to oxidize the organic sulfur compounds present in petroleum [18-20].

Mousa and his team work investigated reducing the sulfur in heavy naphtha using Ni/HY, Zn/HY, Cu/HYand Ni - Zn /HY catalysts. The adsorptive of sulfur was carried out in different operating conditions in a batch process. The maximum removal efficiency was 56% using (Ni-Zn)/HY catalyst at a 1.2 g dose for 24 h[21]. While, Khalel described the oxidation desulfurization efficiency for AL-Ahdab which was improved by an activated carbon catalyst to 32.8% corresponding to a sulfur content (2.6 wt%). the oxidation/extraction desulfurization improved efficiency (31.5%) at a 3:1 solvent/oil ratio, [22]. Also, in the literature, some of reported research used four Keggin-type heteropoly acids as catalysts and acetonitrile as an extractant to apply the ultrasound-assisted catalytic ozonation method to the dibenzothiophene removal procedure. DBT can be successfully eliminated from simulated diesel under the right operational condition. [19]. A combination of hydrogen peroxide and ozone was used to remove dibenzothiophene from model oil for oxidation desulfurization in an ionic liquid (IL) system. Ozone and the hydroxyl radicals it produced-along with hydrogen peroxide-oxidized DBT. Because of their high polarity, the oxidative DBT products were removed from the IL phase. The desulfurization activity of the IL can be renewed five times without noticeably decreasing.[20].

In this study, the effectiveness of the non-thermal plasma process for the oxidation desulfurization of a model fuel containing benzothiophene and dibenzothiophene were explore Through comprehensive experiments, the crucial operating conditions that significantly influence the progress of the reactions were investigated.

2. Material and Method
2.1 Materials
Benzothiophene (97%) and dibenzothiophene (99%) were obtained from Mackline Company in China. N-hexane (99%) was sourced from Merck in Germany, while acetonitrile (ACN) (99.7%) was obtained from BDH England Company.

2.1.1 Model fuel
A model fuel was prepared by dissolving benzothiophene (BT) and dibenzothiophene (DBT) in hexane to achieve a total sulfur content of 500ppm, with 50% of each BT and DBT.

2.2 Method
1.2.1 Dielectric barrier discharge reactor
The dielectric barrier discharge (DBD) reactor utilized for oxidation desulfurization was comprised of two sections. The first section (plasma section) consists of a crystal-quartz tube, as shown in Figure (1), with an inner diameter of 3cm and a wall thickness of 0.1cm. The inner electrode, made of a copper rod (2 cm diameter), was vertically positioned at the reactor's centerline. There was approximately a 1cm gap between the two electrodes, and the outer electrode was constructed using Type 304 copper wire mesh. To generate high power for the reactor, an external 50 Hz AC power supply was employed, delivering voltages ranging from 9000-11000V (peak values). The input voltage for the plasma generator was supplied by a power supply unit. To control the airflow, an airflow meter was used to regulate the specific flow rate of air pumped into the DBD reactor.

In the following section, 250 mL 2-necked round flasks equipped with a condenser were utilized to prevent sample evaporation. The inner tube of the plasma section was positioned approximately 10 mm above the sample surface.
Plasma was produced when the voltage between two electrodes exceeded the voltage level of air. It could produce new ozone, O_2 and other gases quickly and continuously.
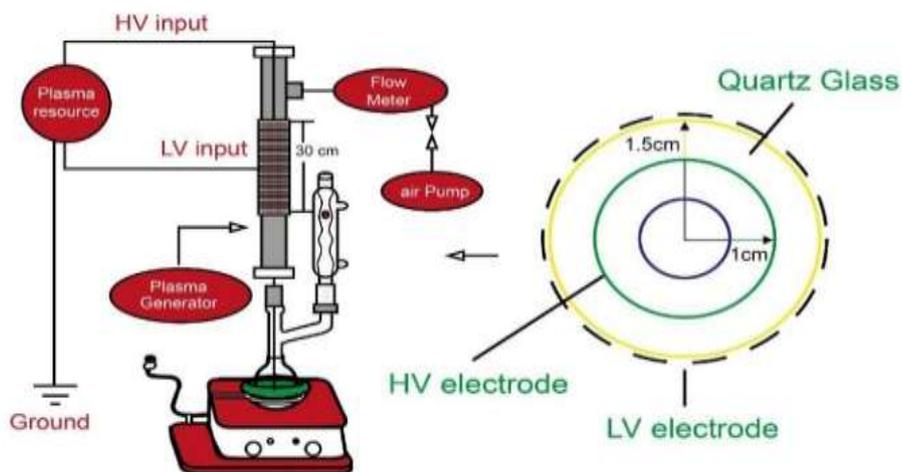
Figure 1: The experimental apparatus of ozone and oxidation desulfurization process

2.2.2 Procedure

The active electrons (e) are generated during the electrical discharge collision with the oxygen molecule and divide into the oxygen atom, collating with the oxygen molecule to produce ozone. Eq. (1), (2).

$$O_2 + e \rightarrow O + O + e \qquad \qquad \dots (1)$$

$$O_2 + O \rightarrow O_3 \qquad \qquad \dots (2)$$

Desulfurization of model fuel is processed in two steps:

Oxidation step: Freshly generated ozone from the DBD plasma was introduced into approximately 50 mL of model fuel contained in the round flask. Concurrently, magnetic stirring was applied to facilitate the oxidation of sulfur compounds for a specified duration. The oxidation process resulted in the conversion of BT and DBT (organosulfur compounds) into polar compounds, specifically benzothiophene sulfone and dibenzothiophene sulfone, as depicted in Figure (2) [23].
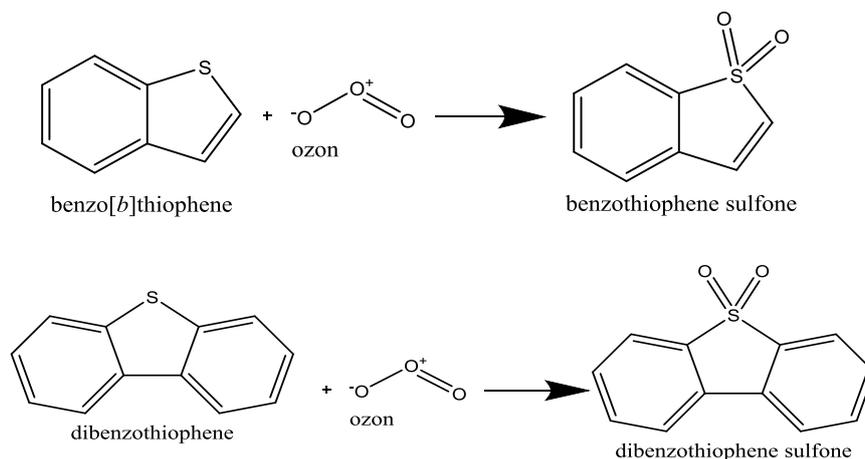
Figure 2: Reaction mechanism of ozone with benzothiophene and dibenzothiophene

Extraction step: The liquid-liquid extraction step was then performed on the treated oil produced from the oxidation step by combining it with the solvent acetonitrile in a 1:1 oxidized oil/solvent ratio (v/v) ratio[24]. The mixture was stirred continuously and kept at room temperature for 30 minutes. After 24 hours, the oil phase was separated from the solvent phase using a separating funnel. The sulfur concentration in the oil phase was determined using the Inductive Coupled Plasma Optical Emission spectroscopy technique at the Petroleum Research and Development Center. The sulfur removal efficiency was then calculated using equation (3).

$$sulfurmoval\ efficiency\ \% = \frac{(Initial\ S\ concetration - \ final\ S\ concentration\ )}{Initial\ S\ concentration} \times 100 \qquad \dots(3)$$

3. Result and Discussion

3.1 Effect of oxidation time

At constant temperature (50°C) and flow rate (75ml/min), sulfur content was studied for a different time (1,2,4,6and 8hr) until the reaction reached equilibrium, as shown in Figure (3). The sulfur removal efficiency was observed to be directly proportional to the reaction time, indicating first-order reaction kinetics as evidenced by the concentration-time plot. From Figure 3, the optimal reaction time was determined to be 4 hours, at which the reaction reached equilibrium.
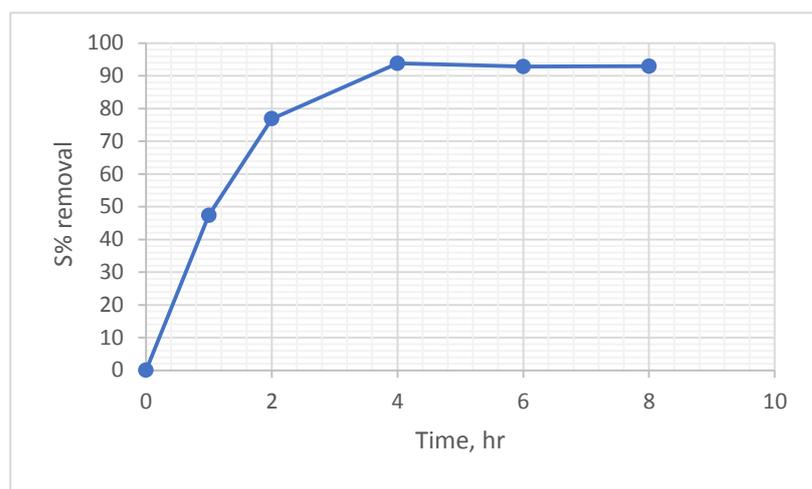
Figure 3- The relationship between sulfur removal (%) and reaction time at a temperature of 50 °C, an airflow rate of 75 ml/min, and a voltage of 11000 volts.

3.2 Effect of the flow rate of air and discharge voltage

The airflow rate supplied to the DBD reactor had a significant impact on the oxidative desulfurization (ODS) process, as illustrated in Figure 4. Increasing the airflow rate resulted in a gradual increase in desulfurization efficiency, reaching a plateau and then declining. When the airflow rate was below 75 mL/min, the amount of air introduced per unit of time was insufficient, leading to lower production of ozone and other reactive oxidants in the reactor. Similarly, when the airflow rate exceeded 75 mL/min, the levels of ozone decreased as the airflow rate increased. The decrease in ozone levels could be attributed to the decomposition of ozone through collision with excess electrons generated by strong discharge voltage or collision with impurities in the air at high flow rates, as well as thermal decomposition as depicted in Equation (4). These factors were the main causes of the observed decline in desulfurization efficiency. However, the optimal conditions for efficient air supply were achieved at a moderate airflow rate of 75 mL/min, creating an ideal environment for sulfur removal. Consequently, the model fuel's sulfur compounds, namely BT and DBT, were predominantly oxidized to their respective oxides. Therefore, a subsequent airflow rate of 75 mL/min was chosen as the best condition for the subsequent experiments.

$$O_3 \xrightarrow{e \; or \; impurity \; or \; heat} O_2 + O \quad \dots \tag{4}$$

The production of activated species (such as ·OH, ·H, ·O, ·HO2, O2, H2O2, O3, etc.) in the desulfurization process is directly influenced by the discharge voltage. Therefore, the discharge voltage plays a crucial role in determining the effectiveness of desulfurization. In

our study, we examined two discharge voltage levels, namely 9 kV and 11 kV. Figure 3 illustrates the impact of discharge voltage on the oxidative desulfurization capability of the model fuel. Notably, the highest treatment efficiency was observed at the discharge voltage of 11 kV.
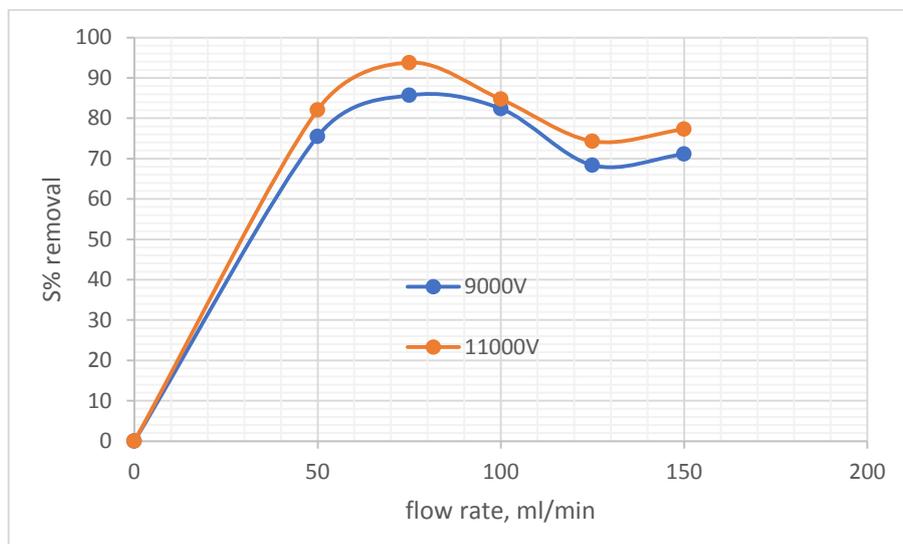
Figure 4: The relationship between sulfur removal (%) and air flow rate at a temperature of 50 ℃, an airflow rate of 75 ml/min, and a voltage of 11000 volts.

3.3 effect of temperature

The performance of the desulfurization process may be affected by the reaction rate. So that, effect of temperature was also studied for different temperature ranges (25, 30, 40, 50, 60and 70℃), as shown in Figure 5. as it noticed that rising reaction temperature from 25 to 50 ℃ performs obviously increasing in sulfur desulfurization efficiency. The sulfur removal significantly increases from 60.73% at 25℃ to 93.78% at 50℃; the reaction rate of oxidation of different sulfur-containing compounds presents in model fuel due to the strong dependence of the reaction rates on the reaction temperature can explain this increase. Although the thermal decomposition rate of the oxidizing agent O_3 increases with an increase in reaction temperature from 50 to 70℃, it has the effect of limiting the rate at which sulfur compounds oxidize. So, the most suitable reaction temperature for the process is about 50 ℃.
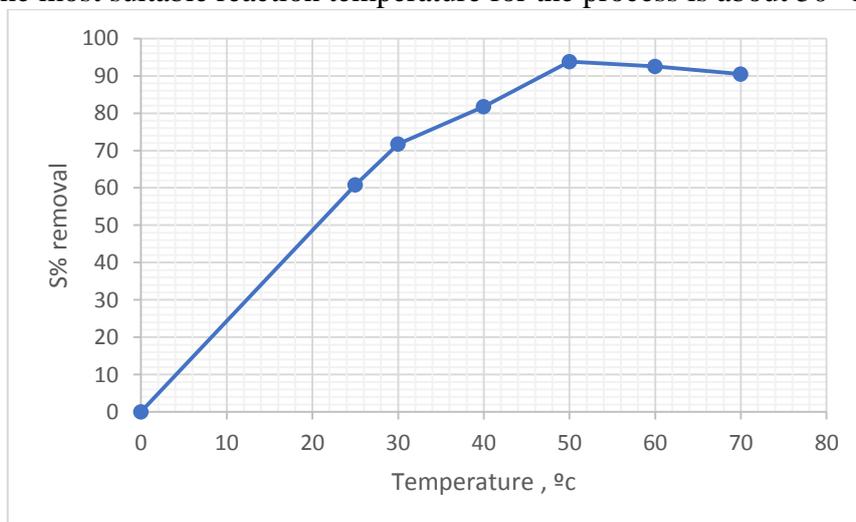
Figure 5: The relationship between sulfur removal (%) and temperature under an airflow rate of 75 ml/min, 4 hrs and a voltage of 11000 volts.

4. Conclusion

To address environmental pollution and industrial challenges associated with sulfur-containing fuel, various desulfurization techniques have been explored, including the application of modern methods such as non-thermal plasma. In this study, the performance of non-thermal plasma was investigated for the oxidation desulfurization of model fuel, with a focus on optimizing the operating conditions. The results showed that the sulfur removal efficiency reached a maximum value of 93.78% under the optimum conditions of 11 kV voltage, 50°C temperature, 75 mL/min airflow rate, and 4 hours reaction time. This non-thermal plasma system can be considered a simple, efficient, and environmentally friendly method for achieving deep desulfurization of fuel.

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