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Deep oxidative desulfurization of model fuel using ozone generated by dielectric barrier discharge plasma combined with ionic liquid extraction

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ABSTRACT

The dielectric barrier discharge (DBD) is often used to prepare ozone. In this study, a novel room temperature oxidative desulfurization method involving ozone oxidation produced in the DBD reactor combined with ionic liquid (IL) [BMIM]CH_3COO ([BMIM]Ac) extraction was developed. The method was suitable for the deep removal of sulfur (S)-containing compounds from model fuel. By this desulfurization technology, 4,6-dimethyldibenzothiophene (4,6-DMDBT), dibenzothiophene (DBT), benzothiophene (BT) and thiophene (TS) were efficiently removed. Normally, the removal of TS and BT from fuel is highly difficult. However, using the proposed method of this study without any catalyst, the removal rate of TS and BT reached 99.9%. When TiO_2/MCM-41 was used as a catalyst, the S-removal of DBT and 4,6-DMDBT increased to 98.6 and 95.2%, respectively. The sulfur removal activity of the four sulfur compounds decreased in the order of TS > BT >> DBT > 4,6-DMDBT.

1. Introduction

Sulfur (S)-containing compounds are undesirable in diesel fuel because the emission of SO_x gases after combustion significantly pollutes the environment and poses risks to human health [1,2]. In recent years, numerous regulations limiting the S-content (<10 ppm) to substantially low levels have been introduced in many countries [3–5]. Thus, a low-cost, high-efficiency, easy-operation, and environment friendly method of achieving ultra-deep desulfurization of diesel fuel must be developed [6].

Diesel fuel is predominantly a mixture of 75% aliphatic hydrocarbons and 25% aromatic hydrocarbons [7]. Thiol, sulfide, thiophene (TS), and its derivatives such as benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are classified as organic S-compounds. BT and its derivatives are more difficult to remove than the others because of their steric hindrance structure.

Various desulfurization techniques such as hydrodesulfurization [5,8,9], extractive desulfurization [10,11], biodesulfurization [12,13], adsorptive desulfurization [14–19], and oxidative desulfurization (ODS) [20–23] have been extensively investigated. ODS method means that S-compounds in the fuels firstly are oxidized into corresponding sulfones and/or sulfoxides, then sulfones and/or sulfoxides are extracted to remove from oil phase using suitable extractants, and ODS method combined with extraction is considered to be one of the most promising alternative methods for deep desulfurization because of its ability to remove BT and its derivatives effectively compared with other processes [24–26]. The oxidation of S-compounds in fuel is a crucial step to desulfurization. The oxidant used most often in ODS is hydrogen peroxide [27]. However, hydrogen peroxide can decompose into water, forming an oil–water biphasic system that affects the fuel quality and results in the difficult recovery of the oil phase. If a gas is used as an oxidizing agent in ODS, oil–water biphasic problems cannot exist.

DBD plasma, which is formed in a strong electric field with low energy and high efficiency, is regarded as a new and promising technology [28,29]. The DBD plasma has been widely used in catalyst modification [30], organic synthesis [31,32], treatment of exhaust gases and wastewater [33,34], and other fields [35–37]. Especially, fresh ozone can be conveniently and continuously produced by DBD plasma in presence of air or oxygen at

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atmospheric pressure [38]. Ozone is a very strong oxidant and can be used to oxidize the organic sulfur compounds in fuel.

In this study, we described a room-temperature oxidative desulfurization system, which attempted to produce ozone generated by wire-cylinder DBD reactor as oxidant to oxidize TS, BT, DBT, and 4,6-DMDBT to their corresponding sulfones and/or sulfoxides. The resulting compounds were then extracted by the IL [BMIM]CH_3COO ([BMIM]Ac). Key factors such as the oxidation time, amount of IL, air flow rate, discharge voltage, extraction time, and extraction temperature that influenced the efficiency of oxidation and extraction were thoroughly investigated.

2. Experimental

2.1. Materials and methods

TS, BT, DBT, 4,6-DMDBT, and IL were purchased from J&K Chemical Ltd. and used without further purification. Model diesel was prepared by dissolving T, BT, DBT, and 4,6-DMDBT in *n*-octane to provide a solution with S-contents of 500, 500, 107, and 94 ppm, respectively. TiO_2/MCM-41 catalyst was synthesized according to a reported method [39].

2.2. Experimental apparatus

Fig. 1 is the schematic of the experimental apparatus for ODS process. The apparatus was mainly composed of a plasma generator (CTP-2000 K, Nanjing Suman electronic Co., Ltd.), a DBD reactor, a mass flow controller, an air compressor, an oscilloscope, and ODS portion. The DBD reactor was, wire-cylinder structure (inner diameter: 19 mm), made of 2 mm thick quartz glass, which was served as a dielectric barrier. Outside of the quartz glass, a layer wire mesh was surrounded as low voltage (LV) electrode, and inside of the quartz glass, a 3 mm thick round steel rod was installed as high voltage (HV) electrode with a discharge gap of about 8 mm between the two electrodes. A variable voltage transformer was connected to the plasma generator to provide the input voltage. Air controlled using mass flow controller was forced into the discharge gap at a certain flow rate, and a digital storage oscilloscope (RIGOL DS1102E) was used to measure the discharge voltage. The discharge voltage was varied from 13.4 to 18.6 kV (peak-to-peak value) with a frequency of 14.3 kHz to change the concentration of ozone generated, and the concentration of ozone was detected according to CJ/T3028.2–94 (Chinese Standard).

2.3. Oxidative and extractive desulfurization procedure

Desulfurization experiments were carried out in 10 mL two-necked flasks equipped with a condenser. Fresh ozone was prepared by DBD plasma, in which air was used as the feed gas. About 3 mL of model oil was added to the flask (for the model oil consisting of DBT or 4,6-DMDBT, 0.01 mg of TiO_2/MCM-41 catalyst was added). Under magnetic stirring, O_3 was injected into the system. After a specific time, the oxidation reaction was terminated, and 0.25 g of IL was added to extract the oxidative products BTO and/or BTO_2. Then, the upper oil phase was periodically collected and analyzed by microcoulometry (WK-2D, Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd., China); the detection limit of the instrument was 0.2 mg L^{-1} and relative standard deviation (RSD) of this method was within ±2%, respectively.

3. Results and discussion

3.1. The example waveform of the voltage at DBD plasma reactor

The example waveform of the voltage was recorded by the digital storage oscilloscope and shown in Fig. 2 at the wire-cylinder DBD plasma reactor when the peak voltage was 16.4 kV. When the discharge voltage applied to the DBD reactor reached the breakdown voltage of the air, a large number of filamentous micro-discharges were generated between the two electrodes, in the meantime blue luminous phenomenon could be observed clearly in the quartz tube. The micro-discharges were randomly distributed on the surface of the inner rod electrode and randomly sprawled to another location in a remarkably short time. Obviously, the waveform of the voltage of DBD was a sinusoidal waveform.

3.2. Effect of the discharge voltage and air flow rate on ozone concentration

Fig. 3 shows the effect of the discharge voltage and the air flow rate on the ozone concentration generated in the wire-cylinder DBD reactor. Mok et al., [40] have reported that the generation

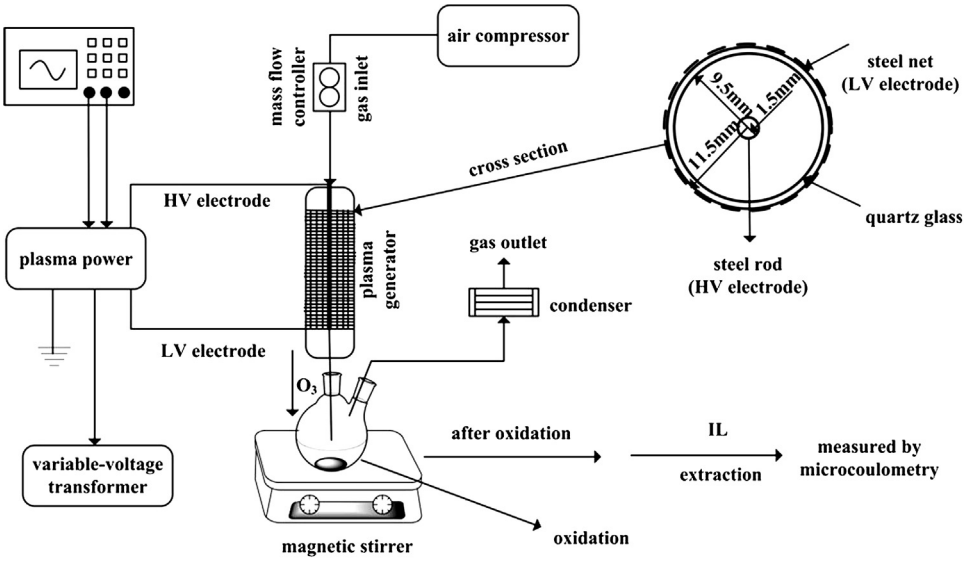

Fig. 1. The schematic of the experimental apparatus for ODS process.