



Oxidative desulfurization of simulated light fuel oil and untreated kerosene

Asghar Molaei Dehkordi*, Zahra Kiaei, Mohammad Amin Sobati

Department of Chemical and Petroleum Engineering, Sharif University of Technology, P.O. Box: 11155-9465, Tehran, Iran

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ABSTRACT

An experimental investigation was conducted on the oxidative desulfurization of model sulfur compounds such as dibenzothiophene and benzothiophene in toluene as a simulated light fuel oil with a mixture of hydrogen peroxide as the oxidant and various acids as the catalyst. The influences of various parameters including reaction temperature (T), acid to sulfur molar ratio (Acid/S), oxidant to sulfur molar ratio (O/S), type of acid, and the presence of sodium tungstate and commercial activated carbon as a co-catalyst on the fractional conversion of the model sulfur compounds were investigated. The experimental data obtained were used to determine the reaction rate constant of the model sulfur compounds and the corresponding activation energy. Moreover, the adsorption of model sulfur compounds on the commercial activated carbons supplied by Jacobi Co. (Sweden, AquaSorb 101) was studied and the effects of different parameters such as temperature, and various chemical treatments on the adsorption of the sulfur compounds were investigated. Furthermore, the oxidative desulfurization of untreated kerosene with the total sulfur content of 1700 ppmw produced by an Iranian refining company (Isfahan refinery) was successfully investigated. These experiments were performed using formic acid as the catalyst and hydrogen peroxide as the oxidant at the mild operating conditions of $T=50$ °C, $O/S=5$, and the $Acid/S=10$. It was realized that about 87% of the total sulfur content of untreated kerosene could be removed after 30 min oxidation followed by liquid–liquid extraction.

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1. Introduction

Environmental concerns necessitate fuels with low sulfur content. The sulfur compounds of fuels not only cause an adverse effect on the quality of petroleum products by decreasing the API gravity, but also are converted into SO_x compounds during the combustion of fuels and, hence contribute considerably to acid rains and air pollution [1–4]. Thus, very stringent regulations for ultra-low-sulfur fuels were imposed on oil refineries to reduce the sulfur content of fuel oils to a very low limit about 10 to 20 ppm [5].

At present, hydrodesulfurization (HDS) is the most widely used industrial process for reducing the total sulfur content of hydrocarbon fuels. This catalytic process is carried out by treating the fuel oils with hydrogen under severe operating conditions including the operating temperature higher than 570 K, and operating pressure about 69 bar. Under these conditions and in the presence of commercial catalysts (e.g., cobalt molybdenum supported on alumina) the sulfur-containing compounds of fuel oils are converted to hydrogen sulfide and the corresponding hydrocarbons [1,2].

Previous investigations have revealed that the sulfur-containing compounds remaining in treated fuels after the HDS process at sulfur concentrations lower than 500 ppm are typically thiophenic compounds such as dibenzothiophene (DBT), benzothiophene (BT), and

their derivatives. These sulfur-containing compounds have less reactivity to the HDS process and, thus, this process is not effective for these heterocyclic sulfur-containing compounds, or at least needs severe operating conditions, which affect the process economy. Hence, several new processes including the selective adsorption, biodesulfurization, and oxidative desulfurization (ODS) followed by extraction [4,6,7] have been developed to remove satisfactorily these refractory sulfur compounds. In the adsorption process as an alternative process or complementary stage for the HDS process, the untreated refractory sulfur compounds can be selectively removed by an adsorbent at low temperatures and at ambient pressure. In addition, this method is more attractive because it is a low-energy demand process and that the various types of adsorbents are available [8,9]. For example, various types of adsorbents including carbon aerogels [8,10], zeolites (Cu (I)-Y [11], Na-Y [12], etc.), activated carbon [13], organic waste derived carbons [14], etc., have been examined. In addition, developed activated carbons such as $PdCl_2/AC$ [11] or metal-loaded polystyrene-based activated carbons [9] have been used for the selective adsorption of thiophenic compounds.

Oxidative Desulfurization (ODS) as an alternative process to the traditional processes has received much attention for deep desulfurization of fuels for a number of reasons. This is because the ODS process has two main advantages compared to the HDS process. First, the greatest advantage of the ODS process is that can be carried out in the liquid phase and under very mild operating conditions. Second, the most refractory sulfur-containing compounds to the HDS process, (e.g., DBT and its derivatives) show high reactivity toward the oxidation by

* Corresponding author. Tel.: +98 21 66165412; fax: +98 21 66022853.
E-mail address: amolaeid@sharif.edu (A.M. Dehkordi).

this method. According to the ODS process, these refractory sulfur compounds are oxidized to their corresponding sulfoxides and subsequently sulfones. Afterward, these highly polarized products can be removed by a number of separation processes including solvent extraction, adsorption, etc. [6,7,15,16]. Various types of oxidants and catalysts have been examined for the ODS process. Oxidants used include hydrogen peroxide [13,15–18], nitric acid [19,20], nitrogen oxides [19,21], organic hydroperoxides (e.g., tert-butyl hydroperoxide) [22–25], ozone [26], oxygen [27], etc. Hydrogen peroxide is the most widely used oxidant because it is environmentally friendlier. Hydrogen peroxide in the presence of catalysts such as acetic acid [3,18], formic acid [15,17], and polyoxometalate [16] has been used. However, different solid basic catalysts such as polymolybdates supported on alumina [28], V_2O_5/Al_2O_3 and V_2O_5/TiO_2 [29], and Co-Mo/ Al_2O_3 [30] have been also used. The main reasons for the use of hydrogen peroxide as oxidizing agent are: (1) its low cost, (2) non-polluting, (3) non-strongly corrosive, and (4) commercial availability. Nevertheless, hydrogen peroxide is a rather slow oxidizing agent in the absence of acid catalysts. Yu et al. [13] studied the adsorption and oxidative desulfurization of DBT with a mixture of hydrogen peroxide and formic acid in the presence of activated carbon. They have reported that the adsorption capacity of wood-based activated carbons having the specific area ≥ 2000 m^2/g is higher than that of coal-based activated carbons because of their larger specific area. They have also concluded that wood-based activated carbons can be used as the catalyst in this oxidation system. However, they have not stated clearly whether coal-based activated carbons having the surface area of less than 1000 m^2/g could act as the catalyst or not.

In the present investigation, both the adsorption and oxidation processes of DBT and BT in toluene as a simulated light fuel oil were investigated. Therefore, the main objectives of the present study were (1) to examine the removal of DBT from a model solution (i.e., DBT in toluene) by adsorption on activated carbons; (2) to study the oxidative desulfurization of the sulfur-containing compounds (i.e., DBT and BT) from the model solution and also the ODS of an untreated kerosene by means of hydrogen peroxide as the oxidant catalyzed by different acid catalysts; (3) to examine the effects of acid treatment of activated carbons on the adsorption of thiophenic compounds; and (4) to examine the influence of commercial activated carbons having the specific surface area less than 1000 m^2/g on the performance of the ODS process. In fact, one of our main goals in the present study was to explore the adsorption behavior and catalytic role of commercial activated carbons with the low surface area (≤ 1000 m^2/g) for the removal of thiophenic compounds from light fuel oils. It should also be noted that this issue has not been previously investigated.

2. Experimental

2.1. Materials

All chemicals used in the present investigation such as sulfur-containing compounds, i.e., 1-benzothiophene (BT) and dibenzothiophene (DBT), sulfuric acid (95–98%), acetic acid (99%), nitric acid (65%), formic acid (>99%), propanol, sodium tungstate, and potassium permanganate were of analytical grade, which were obtained from Merck Co. (Germany) and were used without further treatment. Hydrogen peroxide with purity of 30 wt.% (Merck product) was used as the oxidant. Two types of activated carbon supplied by Jacobi Co. (Sweden, AquaSorb 101) and Merck Co. (Germany) were used as the adsorbents, which are called “AC-100” and “AC-200”, respectively. These carbons were sieved and the particle size range of 30–50 (U.S. mesh) was used throughout the experimental work. Non-hydrated kerosene with the total sulfur content of 1700 ppm was obtained from Isfahan refinery (Isfahan, Iran) and was used as the feedstock in this study. The health and safety issues concerning the above chemicals used in the present work can be found elsewhere [31].

Table 1

Structural parameters of various activated carbon estimated by the sorption of nitrogen at 77 K

Adsorbent type	S_{ABET} (m^2/g)	V_{Total} (cm^3/g)	V_{Micro} (cm^3/g)	% Mesopore volume
AC-100	945.3472	0.558759	0.308251	44.83
AC-200	1080.5387	0.584425	0.256948	56.03
AC-101	734.4782	0.418100	0.331317	20.76
AC-102	577.4977	0.346105	0.191019	44.81

2.2. Method of analysis

A Perchrom Gas Chromatograph system (GC) coupled with a flame ionization detector (GC-FID) was used to identify and determine the sulfur-containing compounds and their concentrations in both the feed and the treated solutions. A column of 50 m in length \times 0.201 mm in inner diameter, and 0.50 mm in film thickness (HP-PONA) was used for the separation. The carrier gas was helium with the volumetric flow rate of 1.3 mL/min. The temperatures of the injector, oven, and the detector were adjusted at 250, 250, and 280 °C, respectively. Tributyl phosphate supplied by Merck Co. (Germany) was used as internal standard.

Hewlett Packard 5973 GC/MS with Hewlett Packard 6890 GC equipped with a mass selective detector and capillary column HP-5 (cross-linked 5% PhMe silicone, 60 m \times 0.25 mm \times 25 μ m) was used to detect sulfur-containing compounds in kerosene qualitatively. The injector temperature was set at 280 °C with split ratio equal to 20. The initial temperature was set at 50 °C for 5 min and then the temperature was increased to 275 °C with the temperature slope of 2 °C/min.

Total sulfur content of kerosene samples was measured by the lamp method (ASTM D1266-07), which is a standard test method for the total sulfur content of petroleum products.

It should also be noted that for each sample, the aforementioned method of sulfur analysis was repeated three times to obtain the average value of the sulfur content.

2.3. Experimental procedures

2.3.1. Adsorption runs

In the present work, equilibrium adsorption studies were carried out by a batch method in which binary solutions containing toluene and DBT or BT were used. The feed solution (3 cm^3) and the desired amount of adsorbent were mixed in a tubular vial of 7 cm^3 equipped with a tiny magnetic stirrer. The vials were then sealed and were placed in a thermostated bath with stirring for the desired equilibrium times. In each experimental run, a control vial with the same amount of solution (3 cm^3) but without any adsorbent was also placed in the same bath in order to minimize the effects of experimental errors on the initial sulfur concentration (C_{S0}). At the end of each experiment, the liquid phases within the tubular vials and the control vial were filtered by means of syringe filters (13 mm GHP 0.45 μ m; Waters Co.) and were analyzed for the concentration of sulfur-containing compounds by GC. The amounts of adsorbed sulfur compounds (i.e., DBT or BT) were calculated by comparing the sulfur content of the filtrate solution with that in the control vial as follows:

$$q = 26.1 \times 10^{-7} \frac{(C_{S0} - C_S)}{W} \quad (1)$$

where C_{S0} and C_S are, respectively, the initial and final concentrations of sulfur in ppmw, whereas W is the amount of adsorbent in g. Prior to the main experiments, a number of preliminary experiments were carried out to find the appropriate stirrer speed and the batch time. To examine the effect of time on the adsorption process and to find the appropriate batch time, several vials with the same amount of adsorbent (0.01 g/ cm^3) and the same initial DBT concentration (500 ppmw S) were placed in a thermostated bath with stirring at 25 °C for 1 h. After each

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