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Adsorptive desulfurization of heavy naphthenic oil: Equilibrium and kinetic studies

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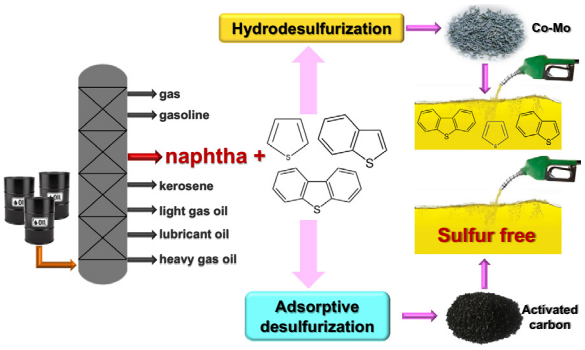
HIGHLIGHTS

- Selective organosulfur compounds removal from synthetic and real naphthenic oils.
- The effect of coexisting inhibitors on the adsorption performance was investigated.
- Carbon activated adsorptive desulfurization capacity was studied.
- Water, carbazole, naphthalene and phenol strongly inhibited sulfur adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Models of adsorptive desulfurization to remove the major refractory sulfur compounds, such as thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) in decahydronaphthalene (DHN), were investigated. The experimental desulfurization of naphthenic oils using activated carbon was conducted in an adsorption system at different temperatures. The adsorptive capacity and selectivity of the adsorbent for sulfur compounds and the effects of coexisting inhibitors on the adsorption performance were examined. The activated carbon showed high capacity and selectivity in the adsorptive desulfurization of naphthenic oil. Water, carbazole, naphthalene and phenol in synthetic naphthenic oil have a strong inhibiting effect on the desulfurization performance of the adsorbent at 100 °C. Increasing the temperature to 150 °C can significantly improve the performance of the adsorbent in the desulfurization of real naphthenic oils. The results showed that the activated carbon exhibited a remarkable adsorption performance. The adsorption capacities reached 1.6×10^{-2}, 2.0×10^{-2} and 1.9×10^{-2} kg kg^{-1} for T, BT and DBT in DHN, respectively. The Langmuir-Freundlich and Toth isotherm models provided good fits with the experimental equilibrium data for the real naphthenic oils. The kinetic results for the real naphthenic oils showed that the adsorption process can be described by a second-order mass transfer model. The results revealed that a temperature increase favors the sulfur adsorption kinetics and there was a greater diffusivity resistance for heavier oils. The data obtained showed effective diffusivity coefficients of between 7.5×10^{-15} and 2.6×10^{-13} m^2 s^{-1} and mass transfer coefficients for the external fluid film ranging from 8.3×10^{-8} to 4.9×10^{-7} m s^{-1}.

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1. Introduction

The desulfurization of fossil fuels remains as one of the most important issues for petroleum refineries due to detrimental environmental impacts caused by the emission of sulfur oxides (Song et al., 2013). In order to reduce the emission of SO_x, regulatory bodies worldwide are increasingly demanding lower levels of sulfur. The EU and the US have limited sulfur level in fuels to less than 10 and 15 ppm, respectively (Fallah et al., 2014). The petrochemical industry has also focused in the production of cleaner fuels due to the recent recession in oil prices, which has led to increased vehicle sales and, consequently, a higher demand for fossil fuels (Lee and Valla, 2017).

Heavy naphtha is a petroleum fraction that forms a major part of commercial gasoline. Its sulfur content varies from 150 to 3000 mg/L depending upon the sulfur content of the crude oil (Nanoti et al., 2011). The strategy used by the oil refining industry to reduce sulfur levels is hydrodesulfurization (HDS). However, this conventional technology is not efficient in the removal of recalcitrant sulfur compounds, such as thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) (Maass et al., 2014). Furthermore, it is a very expensive method due to the high temperature and pressure required as well as the need for high amounts of hydrogen (Nanoti et al., 2011).

Alternative methods have been investigated to substitute or complement HDS including oxidative (Ali et al., 2006; Fallah et al., 2014; Matsuzawa et al., 2002), membrane (Hou et al., 2016), biological (Bachmann et al., 2014) and adsorptive desulfurization (Song et al., 2006) processes. Adsorption is a promising approach to reaching ultralow sulfur levels owing to its several advantages as such hydrogen-free operation, mild operating conditions, and selective removal of recalcitrant sulfur compounds (Farzin Nejad et al., 2013a; Yang et al., 2003).

The selection of an appropriate adsorbent can considerably increase the desulfurization rate. Activated carbons (Selvavathi et al., 2009; Seredych et al., 2009), mesoporous adsorbents (Walcarius and Mercier, 2010; Wu et al., 2012), metal ion-exchanged zeolites (Sundararaman and Song, 2014; Xue et al., 2005), silica gels, and alumina are the most well-known adsorbent materials (Nanoti et al., 2011). Due to the large surface area and pore volume activated carbons are among the most important adsorbents used in desulfurization (Shi et al., 2015).

Although the adsorbent choice and treatment are fundamental for the development of desulfurization techniques, a good understanding of the physical-chemical phenomena involved is also very important. Simulation using kinetics and equilibrium models can reduce the experimental costs and increase the feasibility and precision of process scale-up. There are several models available to describe adsorption equilibrium isotherms, including the Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson and Toth equations (Özkaya, 2006).

For practical purposes, the development of sulfur adsorption processes requires the use of real products and byproducts from petroleum distillation, such as heavy, middle and light naphtha oils (Maass et al., 2015). This paper reports an investigation into the adsorptive removal of thiophenic sulfur compounds from naphtha-range hydrocarbons with activated carbon at different temperatures. The effects of coexisting inhibitors on the adsorption performance as well the adsorption capacity and selectivity of the adsorbent for sulfur compounds were examined. The kinetic and isothermic models that provide the best description of the adsorption process were defined.

2. Experimental

2.1. Naphthenic oils

Synthetic sulfurized naphthenic oils were obtained by adding the sulfur compounds thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) in a wide range of concentrations to a matrix comprised of decahydronaphthalene (DHN). Some classical adsorption inhibitors were considered in this study: water (W), naphthalene (N), phenol (PH) and carbazole (C), representing polar, aromatic, oxygen and nitrogen compounds, respectively. In addition, three types of naphthenic oils obtained by vacuum petroleum distillation were used in this study to determine the effectiveness of sulfur removal by adsorption simulating a real case. In order to vary the sulfur content, hydrotreated streams of the oils were used, due to their absence of sulfur compounds. The non-hydrotreated oil distillates were denominated as LD, MD and HD and the hydrotreated oils as LH, MH and HH, where L, M and H represent light, middle and heavy. Table 1 provides some properties of the non-hydrotreated oil distillates and the hydrotreated oils used in this study.

2.2. Adsorbent

The activated carbon of vegetable origin was supplied by the company Carbomafra, with the specification activated carbon Active 1300 and was manufactured from coconut shell. It was sieved to obtain a grain size of 20–30 mesh (0.595–0.841 μm), which was the range selected for this study. The sample was then washed with distilled water and dried in an oven at 200 °C for a period of 12 h and stored until use.

2.2.1. Adsorbent characterization techniques

Physical characterization of the sorbent particles was carried out through the determination of the real specific mass (ρ_R) and porosity (ε_P) by means of water picnometry and the specific surface area (A_S) by the BET method. The mean diameter (d_m) and apparent specific mass (ρ_A) were obtained by the company Carbomafra applying the methodologies 2854/70 of the *American Standard Testing Methods* (ASTM) and B604-74 of the *American Water Works Association* (AWWA), respectively.

2.3. Adsorption equilibrium studies

Adsorption equilibrium studies for the synthetic and real oils were carried out in a batch system, using closed 125 mL Erlenmeyer flasks. The flasks were placed on a shaker situated inside a thermostatic bath to allow controlled-temperature conditions. To the flasks, ≅10 g of thermally treated adsorbent (M_{ads}) and ≅50 g of fluid phase (M_{f0}) were added.

The synthetic fluid phase composition was obtained by adding sulfur compounds (T, BT or DBT) to DHN in sulfur concentrations varying between 5×10^{-4} and 5×10^{-3} w w^{-1} at 50 °C. The influence of sulfur adsorption inhibitors on the equilibrium was investigated through the individual addition of W, N, C and PH to synthetic naphthenic oil (DBT) at a concentration of 5×10^{-3} w w^{-1} at 100 °C.

For the various sulfur concentrations of the real oils, the fluid phase was obtained by the mixture of each distillate with its respective hydrotreated oil, combining the maximum and minimum sulfur concentrations in the different fractions. These experiments were conducted for a wide range of initial sulfur concentrations at different solution temperatures (50, 100 and 150 °C).