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Single and binary sulfur removal components from model diesel fuel using granular activated carbon from dates' stones activated by $ZnCl_2$

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ABSTRACT

Samples of granulated activated carbon (GAC) produced from dates' stones as adsorbent by chemical activation using $ZnCl_2$ as an activator were used in desulfurization of a model diesel fuel composed of n-decane (n-$C_{10}H_{22}$) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) as sulfur containing compound. The adsorption data were fitted to both Freundlich and Langmuir isotherms to estimate the adsorption parameters. The optimum operating conditions for GAC preparation based on high adsorption capacity using $ZnCl_2$ are $T_{carb} = 600\,^{\circ}C$, $\theta_{carb} = 3.0$ h and $R = 0.5$. Comparison with dibenzothiophene (DBT) adsorption using the same GAC showed that 4,6-DMDBT has a lower adsorption capacity than DBT due to steric effects caused by the existing two methyl groups. Finally adsorption of binary mixtures of DBT and 4,6-DMDBT on GAC were experimentally obtained, fitted and analyzed using extended Langmuir, extended Freundlich and ideal adsorption solution theory, IAST, models.

1. Introduction

Ultra deep removal of sulfur from gasoline and diesel has become very important in petroleum refining industry worldwide due to environmental regulations. The US clean air act amendments of 1990, the new regulations by the US Environmental Protection Agency EPA and government regulations in many countries call for the production and use of more environmentally friendly transportation fuels with low contents of sulfur and aromatics [1]. The EPA Tier II require reduction of sulfur in diesel from 500 to 15 ppmw in 2006 and that in gasoline from 350 to 30 ppmw in 2005 [2].

Sulfur compounds in diesel comprise mainly of alkylated benzothiophene (BT), dibenzothiophene (DBT) and its derivatives. There are about 42 alkylated BT compounds and 29 alkylated DBTs. Among these is 4,6-dimethyl dibenzothiophene (4,6-DMDBT) which has been considered the most difficult to remove [3].

Several studies have been conducted to desulfurize diesel fuel. These researches include various desulfurization methods such as sulfur compounds adsorbents development by complexation [2], van der Waals, electrostatic interactions or reactive adsorption by chemisorption at elevated temperatures [4,5]

Hydrodesulfurization process (HDS) at high temperature (320–380 °C) and high pressure (3–7 MPa) over CoMo or NiMo catalysts is currently a major process in petroleum refineries to reduce the sulfur in diesel fuel. The major sulfur compounds existing in current commercial diesel are the alkyl dibenzothiophenes (DBTs) with one or more alkyl groups at 4 or/and 6 positions which have been considered to be refractory sulfur compounds in the fuel due to the steric hindrance of the alkyl groups in HDS [6]

Selective adsorption of refractory compounds such as DBT and 4,6-DMDBT in liquid hydrocarbon fuels at ambient pressure and temperature have attracted the researchers attention. The great challenge in development of an effective adsorptive desulfurization process is to develop an adsorbent with high selectivity and high capacity of the sulfur compounds and at the same time can be easily regenerated. One of the advantages of desulfurization of fuels by adsorption over conventional HDS is the operation at low temperature. Furthermore, the sulfur content of the fuel can be reduced to a very low level due to removal of the refractory sulfur compounds that cannot be removed by HDS [7,8].

Many attempts were made for various adsorbents such as activated carbon, zeolite 5A and zeolite 13X. Activated carbon is widely used as an adsorbent of organic contaminations due to its porous nature and large specific area. Activated carbon surface structure and properties can be controllable to propose better adsorbents [9]. Activated carbon was studied for refractory compounds desulfuriztion of liquid fuels such as fuel oil [10],

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straight run gas oil [9] and it showed high adsorptive capacity and selectivity for the refractory sulfur compounds such as 4,6-DMDBT.

The reported adsorption capacity of activated carbon for mercaptan, disulfide and thiophene is approximately 0.534 mg S/g while reported charcoal capacity for dimethyl disulfide removal was 15.8 mg S/g [3]. Kim et al. [6] studied adsorptive desulfurization using a model diesel over activated carbon and other adsorbents in a fixed bed adsorption system. They observed that activated carbon shows higher adsorption capacity and selectivity for sulfur compounds with methyl substituent with breakthrough and saturation capacities of 7.15 mg S/g and 16.29, respectively. Haji and Erkey [7,8] studied carbon aerogels as adsorbent for desulfurization of fuels in fuel cell applications. They found that larger average pore size had a higher sulfur rate and adsorption capacity of DBT with 11.2 mg S/g for 4 nm pore size and 15.1 mg S/g for 22 nm.

Recently, DBT removal from model and commercial diesels using granulated activated carbon (GAC) from dates' stone was studies. GAC samples produced from dates' stone and activated by $ZnCl_2$ were used in desulfurization of model diesel containing DBT. 86% of DBT was adsorbed in the first 3 h and 92.6% after 48 h with the optimum operating condition suggested for high adsorption capacity of 700 °C carbonization temperature, 3 h carbonization time and the weight ratio of activator to dates' stone was 0.5. Also, the adsorption data were fitted to both Freundlich and Langmuir isotherms [11].

Binary and ternary mixture adsorption were studied and investigated by many researchers. Noroozi et al. investigated the adsorption cationic textile dyes on GAC and showed that ideal adsorbed solution theory (IAST) gave for binary system of dyes on GAC more accurate predictions than extended Langmuir model [12]. Baciocchi et al. showed that the competitive adsorption of binary chlorophenols on soils using IAST describes satisfactorily the binary system behavior [13]. Alejandro Salaices Avila and Breiter studied the competitive adsorption isotherms of binary system and showed that extended Freundlich model yields better results than extended Langmuir model [14]. Fan et al., proposed a method for simultaneous determination of individual Freundlich equilibrium parameters for binary and ternary phenolic compound mixtures which were consistent with single component equilibrium data [15].

2. Experimental

2.1. Preparation of GAC samples

Dates' stones were obtained from local factories cleaned and washed. Dates stones were then grinded to a size ranges from 1.0 to 2.4 mm. The samples were impregnated in $ZnCl_2$ as an activator following the procedure described elsewhere [11]. Preparation conditions include carbonization temperature, T_{carb} [500–600 and 700 °C], weight ratios of activator to dates' stone, R [0.5 and 2] and carbonization times θ_{carb} [1 and 3 h].

2.2. Nitrogen adsorption measurements

Porous characterization of texture of GAC samples was carried out by physical adsorption of nitrogen at 77 K using an automatic adsorption system (NOVA2200e, Quantachrome). Brunauer, Emmett and Teller (BET) surface area and pore size distribution micro, meso and macroporosity were determined by adsorption/desorption isotherms and using NOVAWin2 data analysis software. $(V_t)_{\mathrm{NLDFT}}$, V_{mic} and V_{meso} are obtained from adsorption isotherm data using the software, where $(V_t)_{\mathrm{NLDFT}}$ is total pore volume estimated using non-linear density function theory (NLDFT), V_{mic} is micropore volume (pore sizes less than 2 nm) determined from NLDFT and V_{meso} is pore volume for pore sizes between 2 and 50 nm and it is taken as the difference between $(V_t)_{\mathrm{NLDFT}}$ and V_{mic}. Also, FT-IR measurements of the GAC samples were performed on a PerkinElmer Universal ATR and data were discussed in [11].

2.3. 4,6-DMDBT GC analysis

For the determination of 4,6-DMDBT in the model diesel a Shimadzu GC 17AATFW-V3 gas chromatograph equipped with Rxi-5ms capillary column, 30 m × 0.53 mm ID (Restek) and FID detector is used. The optimum GC conditions were set as follows: injection port temperature was 260 °C, the column oven temperature was adjusted to 150 °C for 3.4 min followed by heating up to 200 °C with a heating rate of 20 °C/min, detector temperature was set to 250 °C and column pressure at 50 kPa.

2.4. 4,6-DMDBT equilibrium adsorption

A stock sulfur model diesel containing n-decane ($n\text{-}C_{10}H_{22}$) and 200 ppmw S as 4,6-DMDBT was prepared. Known weight of GAC and 10 ml sample of the model diesel fuel is added in 100 ml stoppered conical flasks. Ten of such solution were prepared and placed in an orbital shaker at room temperature. Enough shaking was performed to ensure a reasonably good relative movement between GAC particles and the liquid. At predetermined time a sample was withdrawn, filtered on filter paper and the filtrate was subjected to analysis by GC after addition of known weight of tetradecane as internal standard (IS).

3. Results and discussion

3.1. Textural characteristics of the produced GAC

The average pore size of all GAC samples fall in the range of 1.29–1.88 nm. The specific areas for all samples using the Brunauer, Emmett and Teller (BET) equation are between 802 and 1270 m^2/g. The total pore volumes, V_t, estimated from the adsorption isotherm branch at a relative pressure of 0.98 has a range of 0.44 and 1.65 cm^3/g. More detailed textural characteristics of the produced GAC are available in the previous study [11].

To study the effect of the GAC preparation conditions on the nitrogen adsorption isotherms shape two representative samples, DDS23 and DDS24, were selected. Also, the same samples were used to generate FT-IR spectra to determine the functional group present on the surface on the GAC samples. However, nitrogen adsorption isotherm and the FT-IR spectra were discussed in the previous study [11].

3.2. 4,6-DMBT adsorption

The Langmuir isotherm equation is given by

$$q_e = q_m \frac{a_L C_e}{1 + a_L C_e} \tag{1}$$

where q_e is the amount of solute adsorbed at equilibrium, q_m is the adsorption capacity (mg S/g of dry GAC), a_L is the Langmuir adsorption constant and C_e is the equilibrium concentration of adsorbate in mg/l.

The Freundlich isotherm equation is given by

$$q_e = k C_e^{1/n} \tag{2}$$

where k and n are constants incorporating all the factors affecting the adsorption process such as adsorption capacity and intensity.