



Kinetics of sulfur removal in high shear mixing-assisted oxidative-adsorptive desulfurization of diesel



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ABSTRACT

Current global environmental regulations require deep desulfurization of prevailing high-sulfur crude oil reserves to limit toxic sulfur oxide emissions during fuel combustion. In this study, deep desulfurization of diesel was carried out in two sequential batch steps: (1) oxidation of refractory sulfur compounds in diesel into sulfones and (2) adsorption of the polar sulfur-species in the resulting organic phase onto commercially available adsorbents. Oxidative desulfurization of diesel was performed in a glass vessel equipped with a high shear mixer set at 12,000 rpm. Phosphotungstic acid, tetraoctylammonium bromide and hydrogen peroxide were used as catalyst, phase transfer agent and oxidant, respectively. Adsorptive desulfurization, on the other hand, was carried out using powdered alumina, granular alumina, powdered activated carbon (PAC), and granular activated carbon (GAC) adsorbents. Characterization results showed that powdered alumina and PAC appear to be aggregates of small crystalline structures, with PAC having larger surface area of $846 \text{ m}^2 \text{ g}^{-1}$ compared to powdered alumina at $129 \text{ m}^2 \text{ g}^{-1}$. Micropores were detected in PAC, while the porosity of powdered alumina was attributed to the presence of mesopores. Sulfur removal by the four types of adsorbents conformed to the pseudo-second order model, implying that chemisorption was the rate-limiting step. The computed adsorption capacities from the kinetic model at 3.47, 1.09, 3 and 1.09 mg g^{-1} were in agreement with the experimental adsorption capacities at equilibrium of 3.36, 0.98, 3 and 1 mg g^{-1} for powdered alumina, granular alumina, PAC and GAC, respectively. The 2-line Weber-Morris plots of the four adsorbents indicated the effects of boundary layer diffusion and intraparticle diffusion in sulfur removal. The values of k_{id1} and k_{id2} , as well as I_1 and I_2 , implied that boundary layer diffusion proceeded at a faster rate than the rate-determining step which was intraparticle diffusion. Higher intraparticle diffusion coefficient values were observed for powdered alumina due to its larger particle size and, consequently, smaller surface area where the sulfur compounds tend to be more readily adsorbed.

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1. Introduction

High-sulfur fuel poses increased environmental risks because its combustion in automobiles and industrial operations releases noxious sulfur oxides into the atmosphere (Ogunlaja et al., 2014). Sulfur oxides are known precursors of acid rain, and are reported to cause fuel refining problems, such as catalyst deactivation during

oil processing and corrosion problems in pipeline, pumping, and refining equipment (De Luna et al., 2017). Furthermore, sulfur compounds poison the catalysts for carbon monoxide oxidation and nitrogen oxide reduction in vehicle exhaust catalytic converters (Liu et al., 2017). Because of these considerations, environmental regulations worldwide has imposed ultra-low sulfur concentrations in liquid fossil fuels at 10–15 ppmw for diesel (Mansouri et al., 2014). Stricter policies that will require zero sulfur emissions are even foreseen, giving rise to the need for more development of advanced sulfur removal technologies (Sarda et al., 2012).

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Nomenclature

A	external surface area of the adsorbent (m^2)
C_0	initial sulfur concentration (mg dm^{-3})
C_t	sulfur concentration at time t (mg dm^{-3})
D	intraparticle diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
l	intercept of the line which is proportional to the boundary layer thickness (mg g^{-1})
k_1	pseudo-first order rate constant (min^{-1})
k_2	pseudo-second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$)
k_f	external surface diffusion coefficient (m min^{-1})
k_{id}	intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$)
M	mass of adsorbent (g)
q_t	adsorption capacity at any time t ; the amount of sulfur adsorbed on the adsorbent at any time t (mg g^{-1})
q_e	equilibrium adsorption capacity; amount of sulfur uptake at equilibrium (mg g^{-1})
r	particle radius assuming spherical geometry (m)
t	time (min)
V	volume of the solution (dm^3)

Petroleum refineries are currently being confronted by high-sulfur feedstock due to the ever-increasing demand for petroleum products from the heavy oil fractions and the declining supply of crude oil (Hussain and Tatarchuk, 2013). This poses a problem since conventional hydrodesulfurization (HDS) in refineries requires extreme operating conditions such as high temperature and pressure, along with large amounts of catalysts and long residence times, to remove organic-bound sulfur from fuels (Ho, 2004; Xu et al., 2014). Furthermore, HDS is ineffective in removing highly refractory sulfur species such as dibenzothiophene (DBT) and substituted DBTs (e.g. 4,6 dimethyl-di-benzothiophene) (Dasgupta et al., 2013; Ogunlaja et al., 2014). Thus, the production of diesel fuel with sulfur concentrations below 50 ppm via conventional HDS technology becomes uneconomical (Stanislaus et al., 2010). The problem of deep HDS of diesel streams is also aggravated by the inhibiting effects of co-existing polyaromatics and nitrogen compounds in the feed, as well as by the H_2S in the product (Song, 2003).

Many researches have attempted to develop alternate or complementary processes to conventional HDS, such as adsorptive desulfurization, biodesulfurization, and oxidative desulfurization (Chen et al., 2010). Adsorptive desulfurization is based on the ability of a solid material to physically adsorb organo-sulfur compounds like thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) (Saleh et al., 2017). The efficiency of the desulfurization is determined mainly by the adsorbent properties, such as adsorption capacity, selectivity for organo-sulfur compounds, durability, and regenerability (Babich and Moulijn, 2003). The great challenge in the development of an effective adsorptive desulfurization process is in synthesizing an inexpensive adsorbent with high selectivity for sulfur compounds even at ambient temperature and pressure (Al-Ghouthi et al., 2010). Biodesulfurization involves the removal of organo-sulfur compounds from petroleum using bacteria without compromising the integrity of the hydrocarbon molecules in the fuel (Stanislaus et al., 2010). It offers several benefits to the petroleum industry, such as savings in capital and operating costs, flexibility to handle a wide range of petroleum streams, rapid

engineering and construction time, and safer and milder conditions (Tang et al., 2013). Oxidative desulfurization (ODS), on the other hand, employs oxidizing agents such as hydrogen peroxide to convert sulfur compounds in fuel into sulfones (Chen et al., 2010). In ODS, the electrophilic addition of oxygen atom to divalent sulfur forms unstable sulfoxides, and eventually sulfones in the heterocyclic thiophene ring (Etemadi and Yen, 2007). Due to the difference in the physico-chemical properties, sulfones can be easily separated from the hydrocarbon fuels by solvent extraction, distillation, and adsorption (Sengupta et al., 2012).

Among the non-HDS processes, ODS has drawn significant attention since it can remove sulfur compounds without the need for extreme operating conditions (Yu et al., 2014). The oxidation of sulfur-containing compounds in fuels leads to the formation of sulfoxides or sulfones. The high conversion of sulfides to sulfones and sulfoxides provide the difference in polarity that can be used for selective removal of sulfur (Etemadi and Yen, 2007). The polar sulfones are then separated from the hydrocarbons through suitable separation process such as solvent extraction, catalytic decomposition, or adsorption (Chen et al., 2010; Ma et al., 2007; Stanislaus et al., 2010). The efficiency and economics of ODS is strongly dependent on the method used for separating the sulfones from the oxidized fuels (Nanoti et al., 2009).

Previous studies have explored the utilization of various solid adsorbents on the removal of sulfur from fuel. Murata et al. (2004) achieved nearly 100% sulfur removal of using alumina adsorbents. The reusable properties and the high polar adsorption efficiency of alumina demonstrated by previous studies made it an ideal option for sulfur removal (Chen et al., 2010). Seredych and Bandoz (2010) used polymer-derived carbon to remove dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) from simulated diesel fuel with 20 ppmw total sulfur. Adsorptive desulfurization can supplement HDS process as a polishing step and offers an alternative solution to the high cost of producing ultra-clean fuels (Hussain and Tatarchuk, 2013).

In this study, the kinetics of sulfur removal from real diesel fuel by adsorption onto commercial alumina and activated carbon was investigated. The adsorbents selected were powdered alumina, powdered activated carbon (PAC), granular alumina and granular activated carbon (GAC), and the effects of contact time, adsorbent dosage and kinetics of sulfur adsorption were evaluated.

2. Materials and methods

2.1. Chemicals and adsorbents

The raw diesel fuel used in the experiments was provided by the Tai-Chin Global Company, Taiwan. Tetraoctylammonium bromide ($\text{C}_{32}\text{H}_{68}\text{BrN}$, TOAB, 99%, Sigma-Aldrich), phosphotungstic acid hydrate ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 20\text{H}_2\text{O}$, HPW, 99%, Sigma-Aldrich), and industrial grade hydrogen peroxide (H_2O_2 , 50% v/v) purchased from Hung Yao Instruments Company, Taiwan were used as received. The commercial adsorbents used were powdered alumina (Al_2O_3 , Sigma-Aldrich), PAC, GAC, and granular alumina purchased from a Taiwanese supplier.

2.2. Analytical methods

The morphology and chemical composition of the adsorbent surface were analyzed using a scanning electron microscope (SEM, 200, QUANDA) and an energy dispersive spectroscope (EDS, XM4 Genesis, EDAX), respectively. The adsorbent surface area and related physical properties were determined by a Brunauer-Emmett-Teller (BET) analyzer (2010, ASAP).

Sulfur concentration of all samples was analyzed as total sulfur

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