

Hydrodesulfurization of diesel in a slurry reactor

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ABSTRACT

The need for more complete removal of sulfur from fuels is due to the lower allowable sulfur content in gasoline and diesel, which is made difficult by the increased sulfur contents of crude oils. This work reports an experimental study on the hydrodesulfurization (HDS) of diesel in a slurry reactor. HDS of straight-run diesel using a NiMoS/Al₂O₃ catalyst was studied in a high-pressure autoclave for the following operating conditions: 4.8–23.1 wt% catalyst in the reactor, 320–360 °C, 3–5 MPa pressure, and 0.56–2.77 L/min hydrogen flow rate. It was found that the reaction rate was proportional to the catalyst amount and increased with temperature, pressure and hydrogen flow rate. The reaction kinetics for the HDS reaction in the slurry reactor was obtained. As compared with HDS in a fixed bed reactor, HDS in a slurry reactor is promising because of the uniform temperature profile, high catalyst efficiency, and online removal and addition of catalyst.

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1. Introduction

There is a need for the more complete removal of sulfur from fuels due to the lower allowable sulfur content in gasoline and diesel, which is made difficult by the increased sulfur contents of crude oils (Song and Ma, 2003). Sulfur content in diesel will be limited to 10 ppm in developed countries by the year 2010, while the world-wide average sulfur content in crude oils has increased about 60% from 1981 to 2001 (Li, 2004).

The increasing demand for sulfur removal has required large improvements in deep hydrodesulfurization (HDS) technology. Most HDS processes use fixed bed reactors. Improvements in HDS technology have focused on the development of high activity catalysts, advanced reactor design of multiple bed systems within one reactor, and using new internals or structured catalysts to realize counter-current flow (Song and Ma, 2003; Babich and Moulijn, 2003). However, there are still some disadvantages with performing HDS in a fixed bed reactor. First, the HDS catalysts used in a fixed bed reactor are as large as several mm to limit the pressure drop, thus internal diffusion is a problem that decreases catalyst efficiency (Bruljn and Johannes, 1981; Macías and Ancheyta, 2004; Marroquín et al., 2005). Second, HDS of diesel is strongly exothermic, with $-\Delta H_r \approx 70 \text{ kJ/mol}^{-1}$ (Li, 2004). Most fixed bed reactors use excess cold hydrogen between layers to remove the reaction heat, but an average temperature rising of 40 °C still exists due to the large

reaction heat (Li, 2004). To avoid the harmful effect of a high temperature on the catalyst, a low temperature must be used in the inlet region of the reactor, which decreases the activity of the catalyst. It has also been noticed in the processes of ultra deep desulfurization that the need for a larger amount of cold hydrogen can lead to a large difference in the velocities of the gas and liquid phases. This, in turn, results in phase separation (Li, 2004). Phase separation will decrease the heat transfer rate and results in hot spots and consequently catalyst coking and deactivation. Last but not least, producing clean fuels has become more difficult in a fixed bed reactor due to the ever increasing low grade crude oils.

There has been much experience with slurry reactors in the advanced technology of gas-to-liquid processes, such as Fischer–Tropsch synthesis, methanol synthesis and dimethyl ether synthesis (Wang et al., 2007). For hydrotreating processes, the hydrotreating technology of residual oil with a fluidized bed developed in 1960s is similar to the slurry reactor technology (Furimsky, 1998). Although there is not yet an industrial HDS technology using slurry reactors, slurry reactors have been considered advantageous for HDS processes to produce clean fuels (Furimsky, 1998; Babich and Moulijn, 2003). The advantages of slurry reactors include (Wang et al., 2007): (1) simple construction and lower capital required for a large-scale slurry reactor; (2) good temperature control; (3) large capacity; (4) lower pressure loss that considerably saves compression cost; (5) online removal and addition of catalyst; (6) less catalyst required than in the fixed bed reactor due to the higher catalyst efficiency in a slurry reactor.

This work studied the HDS of diesel in a slurry reactor. The influences of catalyst concentration, reaction temperature, pressure, and

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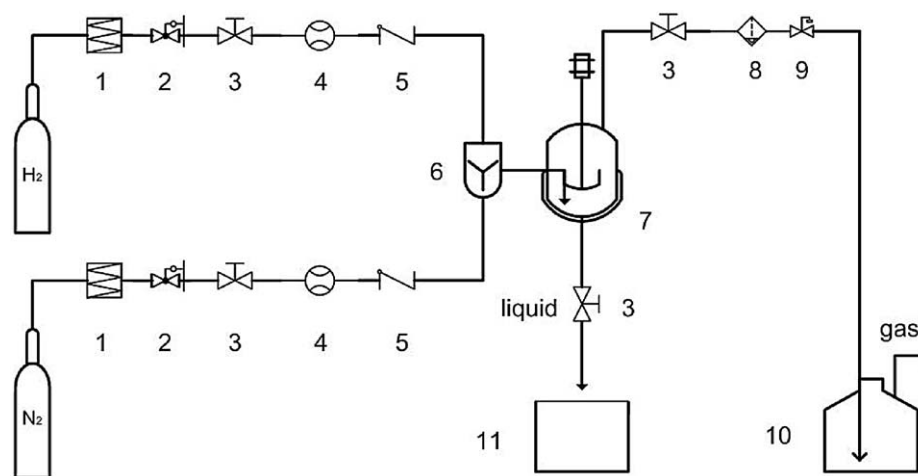


Fig. 1. Schematic of the experimental apparatus for hydrodesulfurization. 1. Filter; 2. Reducing union; 3. Valve; 4. Mass flow meter; 5. One-way valve; 6. Mixer; 7. Autoclave; 8. Gas-liquid separator; 9. Regulator; 10. Exhaust absorption tank; 11. Micro-coulomb instrument.

hydrogen flow rate were studied. A reaction kinetics model was established for the HDS of diesel in the slurry system, which can be used for reactor analysis and design.

2. Experimental

Straight-run diesel from the Shengli oilfield of China was used in the experiments. This has a density 853 kg/m^3 and 2200 ppm sulfur content. A supported $\text{NiMoS}/\gamma\text{-Al}_2\text{O}_3$ catalyst was used with the loading of $\text{NiO}+\text{MoO}_3 \geq 25\%$. When preparing the catalyst, ammonium tetrathiomolybdate aqua solution was used as sulfide precursor and impregnated into the carrier $\gamma\text{-Al}_2\text{O}_3$. The precursor was decomposed in situ under hydrogen pressure to form sulfide catalyst. Thus, there was no need of additional presulfidation of the catalyst. The details could refer to Chai et al. (2007) and Trakarnpruk and Seentrakoon (2007). The particles had an average size of $80 \mu\text{m}$, which was measured with a Malvern particle size analyzer.

The experiments were carried out in a 1.0 L high-pressure autoclave. A schematic of the apparatus is shown in Fig. 1. The pressure was controlled by a regulator valve. The gas flow rate, temperature and stirring speed were controlled by a DCS. The system was purged with nitrogen before each experiment and during the period of increasing the temperature and pressure. Then the gas was switched from nitrogen to hydrogen to start the HDS reaction. The liquid phase was sampled every 10–20 min. The sulfur content of liquid was measured with a non-online micro-coulomb instrument (RPA-200, Jiangsu Jianghuan, analytical company). The sulfur content in the gas phase was calculated from mass balance with an assumption of ideal mixing.

The influences of the catalyst concentration C_{cat} , hydrogen flow rate Q_{H} , reaction temperature T , and pressure P were studied. The ranges of operating conditions investigated were: 4.8–23.1 wt% for C_{cat} , 320–360 °C, 3–5 MPa pressure, 0.56–2.77 L/min for Q_{H} , 500 mL diesel in each batch. The rotation speed of the stirrer was 800 rpm. This rotation speed is high enough to eliminate the effects of gas-liquid mass transfer and catalyst distribution for HDS reactions and particles of $80 \mu\text{m}$ (Aoyi and Maurice, 2008).

3. Results and discussion

3.1. Influence of catalyst concentration

The overall reaction rate is determined by the gas-liquid and liquid-solid mass transfer rates, intrinsic reaction rate and catalyst

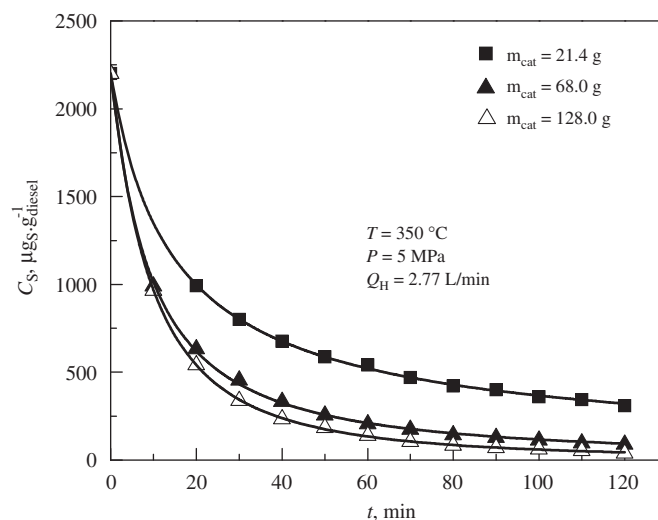


Fig. 2. Decrease in sulfur content for different catalyst concentrations.

concentration. For fast reactions, mass transfer is the rate-controlling step and the catalyst concentration has an insignificant effect on the overall reaction rate. For slow reactions, the overall reaction rate is proportional to the catalyst concentration because mass transfer is much faster than the intrinsic reaction rate. The change in the sulfur content with time-on-stream for different catalyst concentration is shown in Fig. 2. The sulfur content decreased rapidly initially, and then decreased slowly. The reason is two fold. First, the reaction driving force becomes smaller with the decreased sulfur content. Second, different sulfur components are hydrogenated at different rates (Andari et al., 1996). For example, the hydrogenation activity of thiophene is about three orders of magnitude higher than that of the derivatives of dibenzothiophene (Whitehurst et al., 1998). The results also showed that a faster reaction rate was obtained with a higher catalyst concentration. For a further analysis, the specific reaction rate r_{S} was defined as the rate per unit weight, and the results are shown in Fig. 3. In this figure, only data taken with a sulfur content below 800 ppm was considered because the reaction was too fast in the initial period for accurate sampling and sulfur measurement and the initial period was less important because the reaction was much faster at this stage. The results in Fig. 3 showed that the specific reaction rate was almost independent of the catalyst

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