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Study on highly hydrophilic cellulose hollow fiber membrane contactors for thiol sulfur removal

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Abstract

Dispersion-free reactive extraction of thiol compounds from high-sulfur-contained naphtha products into alkali solutions has been studied in a cellulose microporous hollow fiber membrane contactor. A steady extraction was achieved under a long-term operation of 1 month. The constant partition coefficient of thiol in an infinite dilution between the alkali solution and the oil phase was over 940. In addition, the effects of the tube and shell side hydrodynamics on the mass transfer were investigated. The results indicated that the mass transfer resistance in the oil phase boundary layer contributed to more than 95% of the overall mass transfer resistance, while the membrane resistance only accounted for 2% under the operating conditions. The mass transfer flux of thiol extracted from the real naphtha stream containing 883.4 $\mu g\, g^{-1}$ of sulfur came to $2.40 \times 10^{-5}\, kg\, m^{-2}\, s^{-1}$, and the mass transfer coefficient reached $3.91 \times 10^{-5}\, m\, s^{-1}$. The removal efficiency was up to 99% with octane loss less than $3\, mg\, L^{-1}$ when the liquid–liquid volume ratio was 1:1. Furthermore, it was also found that the oil phase flowing at the shell was favorable in fast extraction. A diagram predicting the performance of the contactor for the extraction of sulfur from real naphtha streams was established and the prediction showed a good agreement with the experimental data.

Keywords: Cellulose membrane; Hollow fiber membrane contactor; Thiol sulfur removal; Reactive extraction; Mass transfer

1. Introduction

Environmental regulations are becoming increasingly more stringent with respect to the allowable sulfur level in fuels for internal combustion engines. The presence of sulfur impurities in gasoline is undesirable as the fuel combustion results in the release of SO_2 which are noxious, corrosive, and therefore, present a serious pollution problem. Moreover, sulfur is a well-known poison for catalytic converters, leading to the increase of the volatile organic compounds (VOCs), NOx and total toxic or foul-smelling emissions [1,2]. The sulfur content in motor gasoline has to meet a new sulfur limit of 30 ppm with possible further reduction mandated in the near future. As such, it is imperative to explore new and effective technologies for sulfur removal from gasoline to meet emission standards.

Being one of the main components of motor gasoline, naphtha derived from the fluid catalytic cracking (FCC) process contains a substantial amount of sulfur. The levels of sulfur compounds may be up to 4000 ppm or higher. In order to minimize the hydrogenation of alkanes and octane reduction, the naphtha feed has to be pretreated by selective hydrodesulfurization. Over 75 wt.% of the sulfur compounds are normally present as thiol sulfur in the hydrotreated feed [3], which along with other sulfur compounds such as sulfides, disulfides and thiophenes can be converted to hydrogen sulfide. In the various forms of sulfur compounds, thiol sulfur is of fatal toxicity and its upper limit in the atmosphere should be controlled at a level of lower than 10 ppm.

Although columns and other traditional liquid/liquid contactors have been the workhorses for thiol removal in industry for decades, there exist major drawbacks of phase dispersion because of the two liquid phases to be contacted, and limited mass transfer areas. An alternative technology that is expected to have potential to overcome the disadvantages of the conventional

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equipment is non-dispersive contact via a microporous hollow fiber membrane contactor (HFMC) [4]. In a membrane contactor, the two phases flow on each side of the membrane without phase dispersion, thus avoiding the problems often encountered in the conventional apparatus such as emulsions, foaming, unloading and flooding [5]. The solvent holdup is low, which is an attractive feature when using expensive solvents. Besides, the energy consumption is low and able to treat a large amount of dilute solutions with a small footprint of the equipment. Additionally, the scale-up is more straightforward with membrane contactors.

The attractive characteristics of the membrane contactors have driven considerable research to apply HFMC extraction for the recovery of organic pollutants [6–8], proteins and pharmaceuticals [9,10], volatile [11–15] and non-volatile [16–19] compounds using hydrophobic polypropylene (PP) membranes; and for the separation of alcohols and organic acids or enzymatic transformation using hydrophilic regenerated cellulose hollow fibers or composite flat membranes [20–25].

However, to our best knowledge, there has been rare report on reactive extraction separation of thiol sulfur from petroleum products using HFMCs, especially for using hydrophilic hollow fiber membranes such as cellulose or chitosan membranes. Cellulose is known to be the most abundant organic material [26]. It exhibits remarkable hydrophilic property due to three active hydroxyls in each repeating unit of cellulose molecules, which can be seen from its chemical structure formula in Fig. 1. Because of the strong hydrogen bonds that occur between cellulose chains, cellulose does not melt or dissolve in ordinary solvents, but solvent *N*-metylmorpholine *N*-oxide can physically dissolve cellulose, which was used as the solvent to prepare cellulose membranes via phase inversion method. The details of the membrane preparation can be found elsewhere [27]. It can be seen that the membranes made from cellulose have the characteristics of strong hydrophilicity, solvent resistance and low fouling tendency.

In present work, the separation of thiol sulfur in a simulated naphtha stream using a cellulose membrane hollow fiber contactor has been theoretically and experimentally studied. Based on the quantitative analyses of various mass transport resistances including the oil phase boundary layer diffusion, the membrane diffusion, the aqueous boundary layer diffusion and the interfacial chemical reaction, the dominant resistance and the mass transfer mechanism in the process were discussed. Finally, a diagram prediction for the performance of the contactor to extract sulfurs from real naphtha streams was established and compared with the experimental results.

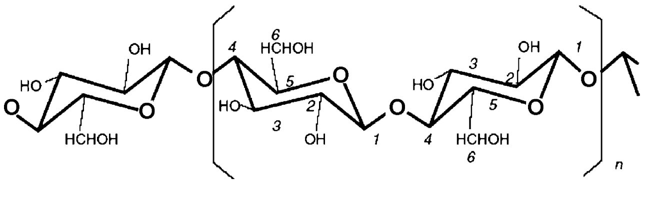

Fig. 1. Chemical structure formula of cellulose $(C_6H_{10}O_5)_n$.

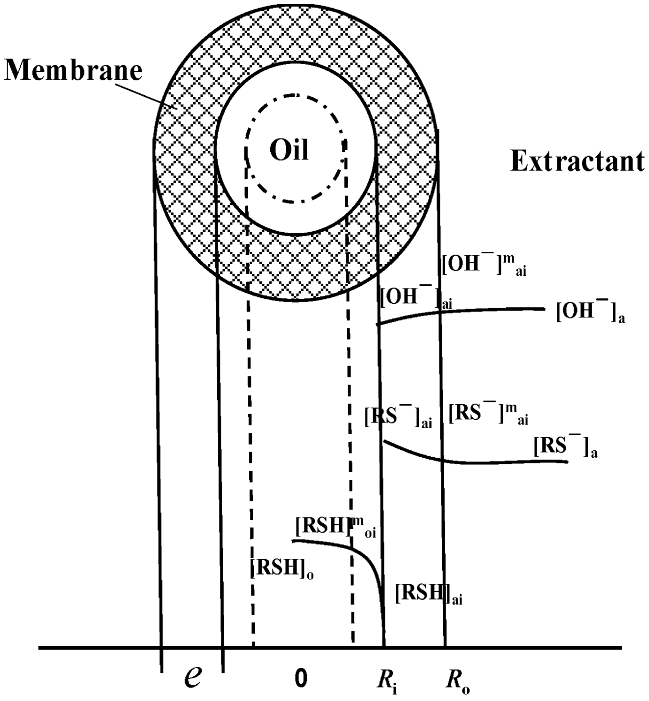

Fig. 2. Concentration profiles of the reactive species in the extraction module.

2. Theory

2.1. Mass transfer with chemical reaction

Membrane extraction is a concentration-driven operation. The mechanism for extracting thiol with aqueous alkali solutions in the cellulose hollow fiber membrane contactor can be illustrated in Fig. 2. Several assumptions have to be made in order to develop the model: (a) the interface is perfectly stable, even at the beginning of extractions when the mass transfer rates are the highest, (b) pore-filling by fluid is uniform throughout the membrane, (c) the two fluids are immiscible with each other, (d) the curvature of the fluid/fluid interface hardly influences the mass transfer, the equilibrium solute distribution or the interfacial area, (e) the partition coefficient of the solute is constant over the concentration range of interest and (f) the mass transfer is described adequately by the simple film type mass transfer coefficients. According to Eq. (1) [28,29], a typical plot can be built up for the solvent concentration varying semi-logarithmically with time and the overall mass transfer coefficient, K_{ov}, can be calculated.

$$\ln\left[\frac{C_e^0/(P-C_f^0)}{(C_e^0/(P-C_f^0))+(V_f/PV_e)(C_f^0-C_f)}\right]$$
$$[1-\exp(((-4K_{ov}V_m)/d_{t\,in})((1/Q_f)-(1/Q_eP)))]=$$
$$t\frac{(1/V_f)+(1/HV_e)}{(1/Q_f)-(1/Q_e)\,\exp[(-4K_{ov}V_m/d_{t\,in})((1/Q_f)-(1/Q_eP))}\qquad(1)$$

During the liquid–liquid extraction, the hypothetical concentration C_f^* in the oil phase is in equilibrium with the actual