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Sulfur removal from gasoline by pervaporation: The effect of hydrocarbon species

Rongbin Qi, Yujun Wang, Jiding Li *, Shenlin Zhu

State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

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Abstract

With the mixtures of different hydrocarbons and thiophene making up the model gasoline, PDMS membrane was used for sulfur removal from gasoline by pervaporation and the impact of different hydrocarbon species on the desulfurization efficiency was investigated experimentally. Experimental results of a series of alkane/thiophene mixtures indicated that, the total fluxes decrease with increase of carbon number in the alkane, while the enrichment factor of thiophene increases simultaneously. With the membrane having a normalized PDMS layer of 15 μm, the total flux for *n*-octane/thiophene mixture was measured to be about $1.04\,\mathrm{kg\,m^{-2}\,h^{-1}}$, with the corresponding enrichment factor of thiophene 4.4 at 31 °C. Compared with alkanes, one or more double bonds in olefin molecules would provide them with a plane geometry and certainly facilitate their transport through the dense membrane. Pervaporation results of *n*-hexene/*n*-hexane/thiophene demonstrated that, the rise of concentration of *n*-hexene in the feed leads to a larger total flux, but a smaller enrichment factor for thiophene at the same time. In addition, the similar framework and electronic properties of aromatics and the coexisting aromatic sulfur heterocycles would result in negative influence for this desulfurization process. Experimental results indicated that, with the increase of the content of toluene in toluene/*n*-octane/thiophene mixtures, the total flux would increase while the enrichment factor of thiophene would decrease. For this system, the coupling effect should be taken into consideration for the further understanding or mathematical simulation of the transport process.

Keywords: Pervaporation; Sulfur removal; Gasoline; Hydrocarbon species

1. Introduction

Increasing concerns on air pollution have led many countries to adopt more stringent regulations which impose an ultra-low concentration of sulfur in gasoline. Usually commercial gasoline is made up of different blending components coming from reforming, coking, isomerization and fluid catalytic cracking (FCC) process. Among them, FCC gasoline, which represents 30–40% of the total gasoline pool, is by far the most important contributor of sulfur. It is so because the atmospheric residues or the vacuum distillates which constitute FCC feedstocks contain significant amounts of sulfur, up to 0.5–1.5 wt.% [1]. The most significant classes of organosulfurs present in FCC gasoline include thiols, thiophene and its light alkyl derivatives and benzeothiophene. Most of them are the results of the direct transformation of the sulfur compounds in the feedstock or the recombination of FCC products. The traditional hydrodesulfurization (HDS) process is highly efficient in removing thiols, sulfides and disulfide, but less efficient for thiophene and the derivatives thereof for the very low reactivity of those refractory species under conventional conditions. Another challenge comes from the great quantity of olefins in FCC gasoline, which provides a fairly good octane number for gasoline but is prone to be saturated in the hydrating process.

The use of common separation process such as distillation alone is inappropriate and/or energy-consuming for desulfurization of gasoline because of the very low content of organosulfurs and the ultra complex components therein. Aiming at capital-avoiding technology for sulfur removal without significant octane loss and without high consumption of limited hydrogen supply, novel non-HDS methodologies are rapidly developed and moving toward commercial levels, i.e., adsorption process [2–4], liquid–liquid extraction process [5,6].

As a membrane-based separation technique, pervaporation selectively evaporates one or more desired components of a

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* Corresponding author. Tel.: +86 10 62782432; fax: +86 10 62770304.
E-mail address: lijiding@mail.tsinghua.edu.cn (J. Li).

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liquid stream by a membrane, which is in direct contact with the liquid mixture. Compared to traditional separation processes such as extraction and distillation, pervaporation offers many advantages, including high separation efficiency, energy saving and simple operation [7]. Pervaporation has been proven applicable for liquid mixtures which are difficult to separate or purify, such as close boiling, azeotropic, isomeric and ultra composition-asymmetric mixtures. Currently, commercial applications of pervaporation fall into two groups: one is the dehydration of alcohols and other solvents and the other is the removal of trace volatile organic substances from water [8]. In recent years, pervaporation has been proven to be a feasible route for the removal of sulfur impurities out of gasoline by different authors [9–11], which allows refiners to minimize their capital investment and operating cost and maximize their processing flexibility at the same time.

PDMS membrane has been extensively investigated for the separation of various mixtures [12,13], and attempts have been made to modify PDMS membrane in different ways to enhance the pervaporation performance [14,15]. Semi-organic bonds in PDMS provide highly flexible backbone with large bond angle, long bond lengths and extreme freedom of rotation, which leads to an increasing free volume for the diffusion of the permeate molecules. In our earlier work [16,17], the PDMS/PAN composite membranes were prepared to separate alkane/thiophene mixtures and shown to be thiophene selective. However, FCC gasoline contains usually not only alkanes, but also aromatic hydrocarbons and olefins. The aromatics have the framework and electronic properties similar to those of coexisting aromatic sulfur heterocycles. Compared with alkanes, the olefins are characterized by one or more double bonds and have therefore a plane geometry which favors their transport through the dense membrane. In view of the common features shared by the thiophenic compounds and aromatic and olefinic compounds, this paper brings further understanding of the effect of the existence of aromatics and olefins on the fluxes and selectivity of this thiophenic sulfur removal process.

2. Experimental

2.1. Membranes

PDMS, ethyl orthosilicate, dibutyltin dilaurate, *n*-heptane were used for the preparation of the membranes, and asymmetric microporous PAN membrane was employed as supports. Firstly, PDMS prepolymer, crosslinking agent ethyl orthosilicate and initiator dibutyltin dilaurate were dissolved into *n*-heptane at ambient temperature. After degassing under vacuum, the solution is cast onto the PAN membrane to form the skin layer. Then the membrane was vulcanized under room temperature to evaporate the solvent and thereafter introduced into a vacuum oven to complete crosslinking. The morphology of the membrane was observed by a scanning electron microscope (Hitachi S-450). As can be seen in Fig. 1, the originally porous surface of the PAN substrate was covered by a flat faultless PDMS layer. The top PDMS layer, functioning as the basis of permselectivity, had a nonporous and tight structure. The thickness of the top skin layer of the membrane was determined by means of SEM photographs [16].

2.2. Separation performance measurement

A representation of the pervaporation apparatus used in this work is shown schematically in Fig. 2. The membrane is supported by a porous sintered stainless steel in the permeate side of the membrane cell. The effective area of the membrane was $2.83 \times 10^{-3}\ \mathrm{m}^2$. The feed liquid, contained in a large tank ($2.5 \times 10^{-3}\ \mathrm{m}^3$) which allowed the determination of the fluxes at nearly constant concentration, was pumped through the feed compartment, where it came into direct contact with the PDMS

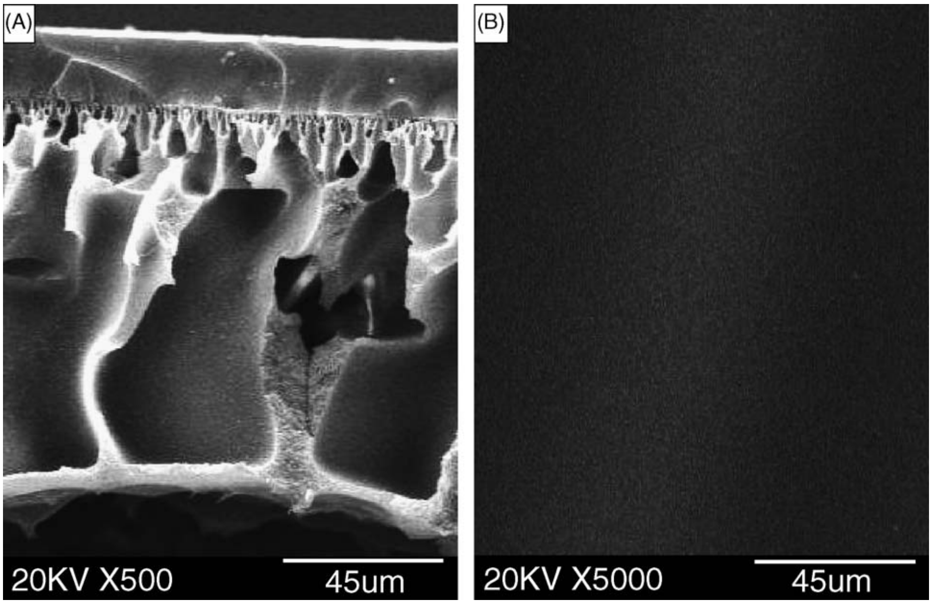

Fig. 1. SEM photographs of the PDMS/PAN membrane: (A) cross-section; (B) top surface.