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Selection and crosslinking modification of membrane material for FCC gasoline desulfurization

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Abstract

Selection and modification of membrane material is important fundamental research for fluid catalytic cracking (FCC) gasoline desulfurization by membrane process. Solubility parameters of FCC gasoline components and typical polymeric membrane materials were calculated and given out. For thiophene species, which are the primary ones in FCC gasoline, solubility parameters were about 19–21 $(\mathrm{J/cm^3})^{1/2}$, while about 14–15 $(\mathrm{J/cm^3})^{1/2}$ for most hydrocarbon species in FCC gasoline. The distinct difference in solubility parameter between the two typical species was just the key to fulfill the separation. By the study and analysis of solubility parameter theory, pervaporation (PV) performance and membrane preparation, polyethylene glycol (PEG) was determined as the promising membrane material for gasoline desulfurization. In spite of its desulfurization capacity, PEG needs modification for its easier swelling and unstable PV performance. According to the comparison on PV performance of PEG before and after modification as well as the swelling experiments, crosslinking was an effective modification way for PEG membrane applied in gasoline desulfurization. After crosslinking, not only the sulfur enrichment factor increased distinctly, but also the membrane performance was stable which was the most important point for practical application. Sulfur enrichment factor increased with the increase of amount of crosslinking agent and crosslinking time, while total permeation flux decreased. Unfavorable results occurred with exorbitant crosslinking resulted form excessive crosslinking agent and overlong crosslinking time. Since sulfur enrichment factor was for key consideration, 16% of crosslinking agent amount and 60 min of crosslinking time were more practical.

Keywords: Membrane material; Selection; Modification; Pervaporation; Gasoline desulfurization

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1. Introduction

Refiners worldwide are rushing to develop their strategy for economically and reliably meeting clean fuel regulation. Technical development for deep desulfurization of FCC gasoline has attracted increasing attention, on membrane process especially. The references [1,2,3] involved detailed background and previous research introduction to the new gasoline desulfurization technology by PV process.

Little has been reported on the selection and modification membrane material for FCC gasoline desulfurization. Membrane material is the core and key point of the membrane technology for deep desulfurization of FCC gasoline. This project was supported by Science and Technology Risk Innovation Fund of CNPC. In this study, solubility parameters of FCC gasoline components were obtained. Membrane materials selection for gasoline desulfurization were conducted by solubility parameter theory and membrane performance analysis. We will also report the modification of membrane material and the membrane preparation conditions involved.

2. Theory

Solubility parameter (δ) was posed firstly by Hildebrand, which was defined square root of cohesive energy for unit volume molecule. The parameter is important value to characterize the interaction intensity among simple liquids. Solubility parameter method is an important way for membrane materials selection of PV process. Whether or not the membrane can fulfill its separation goal depends on the relative permeation capability of the membrane to components. And the permeation capability of the membrane mainly depends on chemical and physical structure of material. Permeation rate to certain

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compound through certain membrane depends on balance and dynamic state effect, i.e. the assignment of components in free solution and membrane phase as well as flow and diffusion of components. The two effects both are affected by the attraction and repulsive power between permeation components and membrane. Higher attraction results in the increased solubility for permeation components in membrane phase. While ultra strong affinity will lead to membrane swelling. On the other hand, strong repulsive and stereoscopic effect will hind the permeation into membrane phase. In summary, membrane material design using the interaction, including dispersion power (δ_d), polarity power (δ_p) and hydrogen bond power (δ_h), between components and membrane is beneficial.

The δ value of certain substance can be represented by its three components: δ_d, δ_p and δ_h. The relation is expressed by Eq. (1):

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

More proximate of solubility parameter between two substance, better for their mutual solubility. To a ternary system, including component *i*, component *j* and membrane, the component which is expected to preferred permeation should exert strong dissolution performance and have closer solubility parameter with polymer molecule. In despite of the limitations of solubility parameter theory, it is an effect way to estimate the interaction between polymer and solvent molecule and to select membrane materials preliminarily.

3. Experimental

3.1. Materials

Membrane materials were all purchased from the Shanghai Reagent Factory. Gasoline feed was obtained from Shenghua Refinery (China), which were after alkali cleaning process. Table 1 gives the hydrocarbon groups of gasoline feed by gas chromatography (GC) analysis.

FCC gasoline is a complicated mixture and various hydrocarbons have significant influence on the membrane. For the fundamental membrane material selection research of PV in a novel separation system, simple model compounds were used as feed firstly to shield the components disturbance. Once membrane material was determined promising, practical gasoline was used to investigate membrane performance. In this study, two kinds of model compounds feed (binary mixture and five component mixture feed) were used considering the results of Table 1. Binary mixture feed was composed of thiophene and *n*-heptane and feed sulfur content was about 1200 μg/g in control of thiophene. Five component mixture feed was composed of thiophene, *n*-heptane (35 wt.%), cyclohexane (10 wt.%), 1-butylethylene (40 wt.%) and toluene (15 wt.%) according to the practical ration of various hydrocarbons in gasoline and feed sulfur content was about 1200 μg/g in control of thiophene.

Table 1
The GC hydrocarbon group analysis results for gasoline feed

Hydrocarbon groups	Gasoline feed composition (wt.%)
Aromatics	15.57
Alkenes	40.03
Paraffins	32.69
Cyclanes	9.82
Unknowns	1.88

All chemicals used were of analytical reagent (AR) grade from Tianjin Chemical Reagent Factory and used without further purification.

3.2. Membrane preparation

Membrane preparation for unmodified membrane involved (PEG as an example): the PEG polymer was dissolved in *N*-methyl pyrrolidone (NMP) to form a homogenous solution of 12 wt.% polymer at room temperature. The solution, after filtration and degassing, was cast onto polyethersulfone UF membrane. The membrane was placed in an oven at 363 K for some time to evaporate the solvent, and then the membrane was dried at the room temperature in vacuum drying oven at least 24 h. All membrane samples were stored in dust-free and dry environment before used in the pervaporation experiments. The active layer has a thickness of about 10 μm which was obtained from scanning electron microscope (SEM) analysis.

Membrane preparation for crosslinking PEG membrane: the PEG polymer mixed with maleic anhydride as crosslinking agent and trimethylamineas catalyst dissolved in *N*-methyl pyrrolidone (NMP) to form a homogenous solution of 12 wt.% polymer at room temperature. Then, the solution, after filtration and degassing, was cast onto polyethersulfone UF membrane. The membrane was placed in an oven at 363 K for some time to crosslink and to evaporate the solvent, and then the membrane was dried at the room temperature in vacuum drying oven at least 24 h. All membrane samples were stored in dust-free and dry environment before used in the pervaporation experiments. The active layer has a thickness of about 10 μm and then the thickness is same basically for all membranes before and after crosslinking.

3.3. Pervaporation apparatus

The schematic pervaporation apparatus is shown in Fig. 1. The permeation cell is made of stainless steel and the membrane is supported on a porous titanium disc with an effective

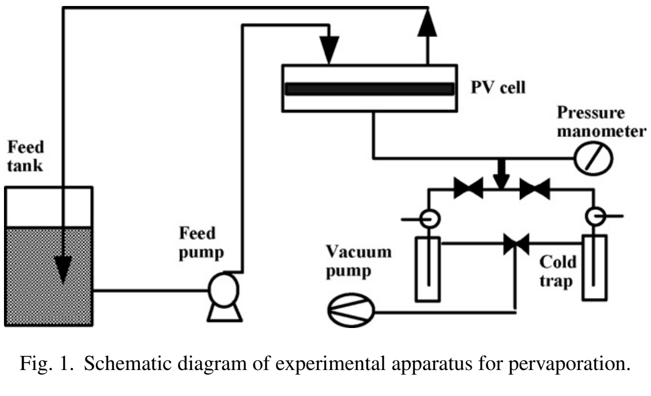

Fig. 1. Schematic diagram of experimental apparatus for pervaporation.