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A review on removal of sulfur components from gasoline by pervaporation

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A B S T R A C T

Desulfurization of gasoline has gained growing importance because of tighter limits of less than 10 ppm sulfur in gasoline in recent regulations. On the other hand, preserving octane rating in gasoline is the most concern subject of the manufacturers. This review focuses on the desulfurization of gasoline by means of pervaporation (PV) process. The process as a new technology has drawn increasing attention and provided an efficient approach for eco-friendly sulfur removal in petrochemical industries due to its high selectivity, feasible economics, and safety. Theoretical aspects in selection of materials for the applied membranes and their modifications are investigated. The various parameters including the type and concentrations of sulfur and hydrocarbon species, feed temperature, feed flow rate, and permeate pressure, which influence the performance of PV are discussed.

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Keywords: Gasoline desulfurization; Membrane separation; Pervaporation; Membrane modification

Contents

1. Introduction	410
2. Membrane separation for gasoline desulfurization	411
2.1. Basics of pervaporation	411
2.2. Membrane material selection	411
2.2.1. Selection of membrane material by solubility parameter theory	411
2.2.2. Membrane material selection by polarity parameter	412
2.2.3. Membrane materials for desulfurization	412
3. Dynamic sorption analysis	413
3.1. Diffusion, sorption and permeation coefficients	414
4. Analysis of the upper bound curve	415
5. Membrane material modifications	415
5.1. Crosslinking	416
5.2. Blending	418
5.3. Filling	419
5.4. Copolymerization	420
5.5. Treated ionic membranes	420
6. Applied composite membranes	420
7. Effects of operating conditions on pervaporation performance	422
7.1. Effect of feed temperature	422
7.2. Effect of feed and permeate pressures	425

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7.3.	Effect of feed composition	425
7.3.1.	Influence of typical hydrocarbon components in gasoline	426
7.3.2.	Influence of typical sulfur components in gasoline	426
7.4.	Influence of feed sulfur concentration	426
7.5.	Effect of feed flow rate	427
8.	Change of gasoline composition during pervaporative desulfurization	427
9.	Commercial units of pervaporative desulfurization	428
9.1.	S-Brane technology	428
9.2.	TranSep™ technology	428
10.	Conclusion	428
	References	429

1. Introduction

Environmental concerns regarding quality of gasoline is one of the most important issues for petroleum refineries. Among the stringent specifications for gasoline, the sulfur content has a high importance. Sulfur limits of less than 30 ppm were introduced for gasoline in most developed countries to meet EPA (Environmental Protection Agency) 2006 regulations (Song, 2003) while new approaches for deeper desulfurization may become necessary in near future (<10 ppm sulfur) (Kaufmann et al., 2000; Song and Ma, 2003; Ito and Rob van Veen, 2006; Wang et al., 2007; Mohammad et al., 2006). Sulfur in gasoline is a main supply of SO_x emissions and is responsible for increased levels of NO_x in exhaust of the vehicles. In addition, it also spoils the low-temperature activity of automotive catalytic converters (White et al., 2004; Qi et al., 2006a).

Commercial gasoline is a complex mixture composed of alkanes, C₅–C₁₄ olefins, cycloparaffins, and aromatics. It is made up from products of isomerization, reforming and fluid catalytic cracking (FCC) units. FCC gasoline, which has a share of 30–40% in the total gasoline pool, is the most important sulfur contributor in gasoline (up to 85–95%). Therefore, sulfur removal from FCC gasoline is the key to deep desulfurization of gasoline (Kaufmann et al., 2000; Song and Ma, 2003; White et al., 2004). Typical sulfur compounds in gasoline include mercaptans (RSH), sulfides (R₂S), disulfides (RSSR), thiophenes, and the derivatives thereof (Song and Ma, 2003; Qi et al., 2006a). Thiophenic sulfur, which enters to FCC gasoline after alkali cleaning process, represents a large fraction of the total sulfur (80% and over) among the sulfur impurities (Lin et al., 2006b). The thiophene compounds and their derivatives have less reactivity. Therefore, it is more difficult to remove them than the other kinds of sulfur compounds (Lin et al., 2009a).

A basic method for removal of sulfur from gasoline is catalytic hydrodesulfurization (HDS). HDS of FCC gasoline is a straightforward way for reducing the sulfur to the levels even below 1 ppm. However, it needs high investment and operating costs, and also there is one big disadvantage; this technology suffers from significant loss in the octane number caused by saturation of olefins. Therefore, more efforts are being made to develop novel non-HDS methodologies (Qi et al., 2007a) such as bio-HDS, selective oxidation, selective extraction, catalytic extraction, alkylation-extraction, improved selective hydroprocessing (Plantenga and Leliveld, 2003), and membrane separation.

Two main biochemical pathways in biodesulfurization have been reported; ring-destructive (degradation) and sulfur-specific (desulfurization). The former is not commercially useful for the petroleum industry because water-soluble sulfur compounds are produced and the carbon skeleton of sulfur

compounds is used by the bacteria, which reduces the fuel calorific value (Mohebbi and Ball, 2008; Mohebbi et al., 2007). The latter is energetically expensive because the carbon skeleton is not mineralized in order to get back the energy invested (Mohebbi and Ball, 2008). There are limitations for industrial application of biological sulfur removal. The metabolism rate of sulfur compounds is slower than the rate of chemical reactions. Moreover, mass transfer from oil/water interface to the microbe is slow (Marcelis et al., 2003). In addition, large amounts of biomass are needed (typically 2.5 g biomass per g sulfur). On the other hand, it is usually difficult to keep biological systems alive under variable input conditions in the refineries. Separation of the cells from the oil can also be difficult (Konishi et al., 2005), and immobilized cells often have lower activity and limited lifetimes (Borole et al., 2002; Gupta et al., 2005).

Oxidative desulfurization (ODS) combined with liquid extraction is considered one of the novel processes to reduce refractory sulfur-containing compounds. However, it is not successful with FCC gasoline due to the high olefinic content that tends to react with oxygen atoms to form epoxides. In the ODS process, the sulfur containing compounds are oxidized using appropriate oxidants to convert these compounds to their corresponding sulfoxides and sulfones. These are preferentially extracted from light oil due to their increased relative polarity. The oxidized and non-oxidized components must be separated from the feed by applying several extraction, washing, absorption, and distillation operations (Ali et al., 2006). This consecutive separation steps makes the process complicated and expensive.

As a non-HDS method, adsorption desulfurization has some problems to be solved. When the selectivity is low, the adsorbents are easy to be regenerated. As the selectivity increases, the spent adsorbents become more and more difficult to be regenerated (Hernandez-Maldonado and Yang, 2004b,c; Hernandez-Maldonado et al., 2004; Salem and Hamid, 1997). Solvent extraction and calcination in the air are two methods to regenerate the desulfurization adsorbents. In regeneration by solvent extraction, it is difficult to separate sulfur compounds from the organic solvents. In the calcination method, sulfur compounds and aromatics are burned out together that can lose heat value of the fuels (Li et al., 2009b).

Compared to the traditional and non-HDS separation processes, membrane separation offers many advantages including higher separation efficiency, lower energy consumption and operating cost, simple operation and control scheme, ease of scaling up and adaptability to changes in process streams (White et al., 2004; Han et al., 2002; Li et al., 2002). These promising advantages make membrane separation an attractive process for many of research in recent studies.

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