Research Note

Influences of Permeate Pressure and Feed Flow Rate on Benzene Removal from Gasoline by Pervaporation

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ABSTRACT

In this work, the effects of permeate pressure and feed flow rate on the performance of a composite polyvinyl alcohol (PVA) membrane in the removal of benzene from gasoline by pervaporation (PV) were evaluated. The results indicate the remarkable effect of permeate pressure on membrane performance as reducing permeate pressure (higher vacuum) from 30 to 3 mmHg causes the total flux to increase from 6.6 to 51.7 g/hrm^2 and from 12.2 to 79 g/hrm^2 at 25 and 35 °C respectively. Furthermore, increasing feed flow rate enhances total flux and diminishes the amount of benzene in retentate (product) only below 1000 ml/min and has a negligible effect at higher flow rates.

Keywords: Pervaporation, Benzene, Gasoline, Polyvinyl Alcohol, Flow Rate

INTRODUCTION

The removal of benzene from gasoline is an important environmental concern of the petroleum industry. New regulations limit the benzene content of gasoline to an annual refinery average of 0.62% by volume by 2011. In most refineries, the catalytic reformer represents the major source of benzene in the gasoline pool [1]. Various conventional techniques such as distillation, solvent extraction, and use of solid adsorbents can be used to selectively remove benzene from gasoline. However, distillation is not suitable, primarily because benzene forms low boiling azeotropes with normal hexane and naphthenics such as methylcyclopentane and cyclohexane. Alternatively, the extraction of benzene with a solvent such as sulfolane is technically feasible, but presents some disadvantages, including the use of special equipment to compensate for the corrosiveness of sulfolane. Also, desorption step in adsorption-based separation processes presents difficulties [2]. Under such circumstances, quite a number of novel processes have emerged for benzene removal from gasoline. Pervaporation (PV) is one of the most developed membrane technologies considered to be a promising alternative to conventional energy intensive

technologies, economical, safe and eco-friendly. PV is derived from combining permeation and evaporation, the two mechanisms involved in the process. In this process, the components of a liquid feed permeate through a dense membrane and evaporate into downstream at different rates. The driving force for the process is the difference between the chemical activities of the components in the feed and the permeate. Separation occurs because of the different rates of sorption and diffusion of the feed components through the membrane [3]. In recent years, the removal of aromatics from aliphatics, especially benzene from cyclohexane, using pervaporation has received considerable attention. Most studies have focused on the effects of different parameters, including feed temperature, concentration, and membrane type on membrane performance in the separation process [4-7]. Though benzene removal from gasoline has been dealt with to a limited extent by pervaporation using polymeric and cation exchange membranes [1,8], the influence of effective parameters such as permeate pressure and feed flow rate on membrane performance have not yet been investigated. In the present work, the effects of these two parameters on the performance of a composite PVA membrane in the reduction of benzene in gasoline from Tehran Oil Refinery have been studied.

EXPERIMENTAL PROCEDURES

The schematic diagram of the experimental apparatus is shown in Figure 1.

In the pervaporation experiments carried out, the feed mixture was circulated from the feed tank through the cell using a peristaltic pump. The membrane used was supported on a porous stainless steel disc with an effective membrane area of 177 cm^2 embedded in a stainless steel plate and frame from Sulzer Chemtech. The membrane was a composite one with a top layer of PVA on a polyacrylonitrile (PAN) porous support. The feed (gasoline) with a benzene content of 3.1 wt.% was

obtained from Tehran Oil Refinery. Before starting the PV experiments, the test membrane was equilibrated for about 4 hrs with feed solutions. The feed side of the membrane was at atmospheric pressure and the other side (permeate side) was maintained at a pressure range of 3-30 mmHg using a vacuum pump. During the experimental runs, the feed temperature was constant at 25 or 35 °C. A temperature probe attached to the feed tank was used for monitoring temperature during each run. Feed flow rate was changed using a feed pump from 200 to 1200 ml/min. Feed flow rates for the experiments concerning permeate pressure were fixed at 1.1 l/min.
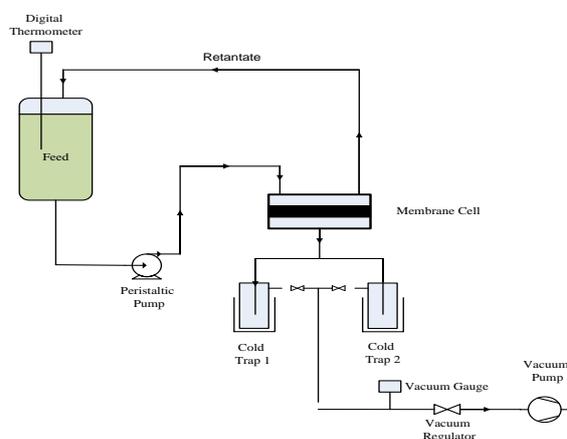

Figure 1: Schematic diagram of experimental apparatus.

The permeate side of the membrane was connected to cold traps immersed in a liquid nitrogen bath. The experiment time was 8 hours in all the cases.

The PV experiments were repeated three times to check for repeatability. Repeatability, expressed as relative standard deviation, ranged between 2.5 and 4.5%. Permeate total fluxes (g/hr.m^2) were determined by weighing the permeate obtained during a certain period of time using Equation 1:

$$J = \frac{Q}{At} \qquad (1)$$

where, J is the permeate flux; Q stands for permeate weight and A is the membrane area; t represents operation time [9]. The analyses of the

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product were performed using a Varian 3800 gas chromatograph equipped with an FID detector and a capillary column (Length: 50 m, inside diameter: 0.23 mm, stationary phase: CP SIL-5, injection temperature: 250 °C). Benzene concentration in the composition was determined using an internal standard.

RESULTS AND DISCUSSION

Effect of Permeate Side Pressure

Permeate pressure is an important operating parameter as high vacuum corresponds to high energy cost. Moreover, achieving low pressures is usually difficult and requires higher energy consumption in comparison with increasing temperature [10]. Thus, for the optimization of PV, the investigation of permeate pressure effect on membrane performance in benzene removal from gasoline seems necessary. In Figure 2, total flux is plotted versus permeate pressure. As shown, the variation of permeate pressure from 30 to 3 mmHg remarkably increases total flux. In other words, reducing pressure increases the permeation rate of components into the membrane and thus improves membrane performance in the removal of benzene from gasoline.
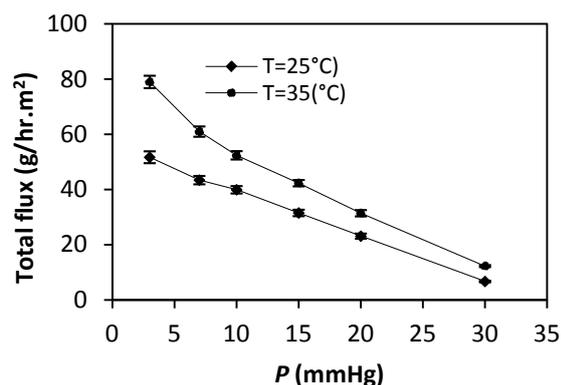

Figure 2: Effect of permeate pressure on total flux (Feed flow rate: 1.1 l/min, feed benzene content: 3.1 wt. %).

Changes in flux variations by pressure depend on thermodynamic properties of organic constituents such as saturated vapor pressure and activity coefficient.

In pervaporation processes, the driving force is provided by the vapor pressure difference between the feed and permeate sides of the membrane. Reducing permeate pressure leads to an increased driving force and consequently enhances total flux. Furthermore, on the basis of Fick's law, the activities of permeates dissolved in the downstream layer of the membrane are increased by increasing permeate pressure. Therefore, activity gradients across the thickness of the membrane are declined and permeate flux drops. The effect of permeate pressure on selectivity is more complicated. Selectivity can be increased or decreased by increasing permeate pressure depending on the relative vapor pressure of the permeating components [11]. Usually, if the faster permeate is less volatile, selectivity declines as permeate pressure increases, while in the case of the faster permeate being more volatile, increasing permeate pressure may make the selectivity increase. Since selectivity has been correctly defined only for two component mixtures in pervaporation processes, in this work, benzene concentration in the permeate has been considered as a criteria for the membrane selectivity. As shown in Figure 3, at permeate pressures of over 20 mmHg, selectivity decreases, whilst at lower pressures, the variation of permeate pressure has a negligible effect on benzene concentration in the permeate.
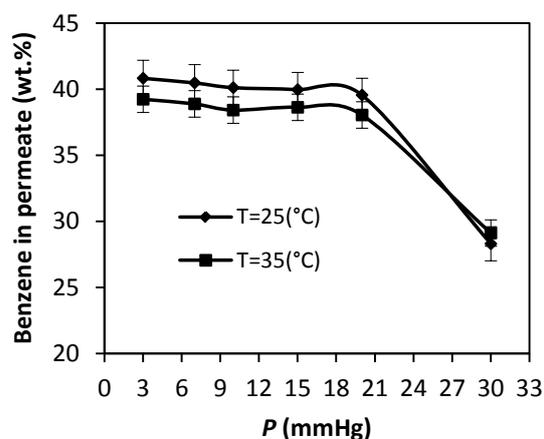

Figure 3: Effect of permeate pressure on benzene content in permeate (feed benzene content: 3.1 wt. %, feed flow rate: 1.1 l/min).

However, gasoline consists of different hydrocarbons with various boiling points. Therefore, the evaluation of pressure effect on membrane selectivity is difficult. However, although variations in the permeate pressure at low pressures have a negligible effect on membrane selectivity, as shown in Figure 4, lowering pressure causes benzene concentration in the retentate to decrease and thus enhances membrane performance. This results from the considerable increase in flux as higher vacuum is applied.
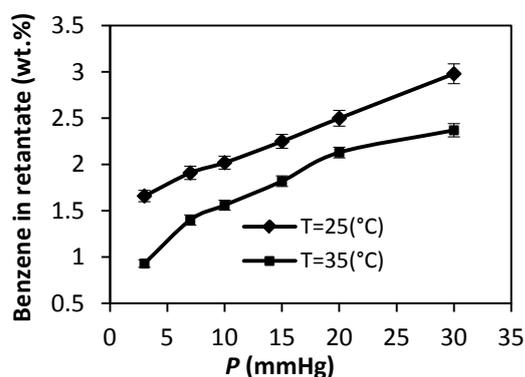

Figure 4: Effect of permeate pressure on benzene content in retantate (feed benzene content: 3.1 wt. %, feed flow rate: 1.1 l/min).

Effect of Feed Flow Rate

In pervaporation processes, the components of the feed mixture permeate through the membrane at different rates. Thus the concentration of the non-permeating component increases at membrane surface and a concentration gradient is formed in the fluid adjacent to the membrane surface. This concentration gradient between the more concentrated boundary solution and the less concentrated bulk is called "concentration polarization" [12] and in many cases lowers membrane performance. The most direct technique to minimize concentration polarization is increasing the feed flow rate past the membrane surface. Figure 5 shows the effect of the feed flow rate on the benzene flux to total flux ratio, when the feed flow rate varies in the range of 200-1200

ml/min at a feed temperature of 35 °C and a permeate pressure of 10 mmHg. As observed, at flow rates below 1000 ml/min, increasing flow rate from 200 to 600 ml/min increases the ratio of benzene flux to total flux, while the flow rates of over 700 and specially 1000 ml/min have a negligible effect on the ratio of benzene flux to total flux.
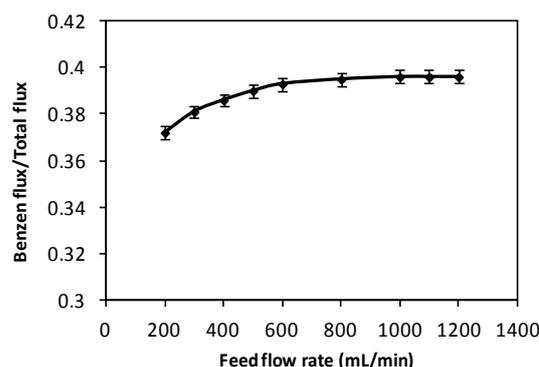

Figure 5: Effect of feed flow rate on benzene flux to total flux ratio (feed temperature: 35°C, permeate pressure: 10 mmHg.

Therefore, only at lower flow rates does concentration polarization affect membrane performance in the removal of benzene from gasoline by a PVA membrane.

Accordingly, with increasing flow rates, the thickness of boundary layer remarkably decreases. This situation causes concentration polarization to diminish on the upstream surface of the membrane. Nevertheless, the examination of Figures 4 and 5 shows that variations in benzene content in the retentate is appreciable as the permeate pressure increases in comparison with flow rate; however, the effect of flow rate on the ratio of benzene flux to total flux, which determines benzene content in the retentate, is small. In other words, the permeate pressure is a much more effective parameter than the feed flow rate. Therefore, in development and upscaling of benzene removal from gasoline using PV processes, optimizing the applied vacuum is of great importance in order to make the process more economically feasible.

CONCLUSIONS

The membrane used herein exhibits preferential permeation to benzene in comparison with other compounds in gasoline as the amount of benzene is reduced from 3.1 wt. % in the feed to below 1 wt. % in the retentate. Increasing feed flow rate improves the membrane performance only below 1000 ml/min and has no appreciable effect at higher feed flow rates. This observation confirms that, in addition to a membrane resistance, an additional resistance, originally from the boundary layer at the membrane interface, dominates the pervapotation performance in the process at a lower feed flow rate.

The effect of permeate pressure on membrane performance is appreciable in comparison with feed flow rate such that increasing vacuum results in a highly increased flux and an improvement in membrane performance. However, at pressures below 20 mmHg, the changes in the permeate pressure do not appreciably affect membrane selectivity to benzene. Therefore, given the high cost of the process at lower pressures and considering the experimental results in this work, in order to scale up the PV process, pressure optimization requires the calculation of mass and energy balances and process equipment.

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