ELSEVIER

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 44 (2012) 662 – 665

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[OD56]

Olefin/paraffin separation using ceramic hollow fiber membrane contactors

R. Faiz*[1], M. Fallanza[2], I. Ortiz[2], K. Li[1]

[1]*Imperial College London, UK,* [2]*University of Cantabria, Spain*

The separation of olefins from paraffin gas mixtures has been the focal point of many researchers and industrial firms [1]. Paraffins such as propane are commonly used as a fuel for engines, industrial processes, and residential central heating, while propylene is a raw material for a wide variety of products including polypropylene which is used in packaging and other important applications such as textiles, laboratory equipment, and automotive components. However, olefins and paraffins are usually produced together as byproducts from natural gas and petroleum refining processes. As a consequence, the separation of light olefins from their respective paraffins is a task of primary importance to the petrochemical industry. Unfortunately, this separation is very challenging due to the similar physical and chemical properties of olefins and paraffins such as molecular size, volatility, and solubility. The separation process is primary carried out by cryogenic distillation in a single or double column process consisting of 150-200 trays at operating temperatures between 183-233 K and pressures of 16- 20 bar. Nevertheless, the energy and capital input of the cryogenic distillation process is considered enormous and has been intensively looked into for possible replacements [2].

In the past few decades, the use of hollow fiber membrane contactors for olefin/paraffin separation has been extensively studied [3,4]. The separation is carried out by the absorption of olefins into an aqueous or organic media containing transition metals ions due to the well-known pi-complexation [5]. However, paraffins do not interact with the absorbent solvent and exit the membrane module in a pure form. The rich olefin-solvent stream may be regenerated where olefins are recovered and the absorbent medium could be recycled back to the membrane module for further absorption. This type of process offers several practical advantages including high surface area per unit contactor volume which contributes significantly to the reduction of the unit size. In addition, operating drawbacks occurring in conventional absorption columns and spray towers such as flooding, loading, weeping, or foaming do not take place in hollow fiber membrane contactors due to the independent control of gas and liquid flow rates [6].

However, one of the major issues associated with the use of conventional polymeric membrane contactors is the long-term stability of the membranes due to wetting [7]. Once wetting phenomenon occurs, the solvent may affect the membrane properties due to particle deposition where pores blockage occurs, or due to the increase in pore size distribution due the membrane’s incompatibility with the chemical solvent. In both cases, the membrane should be frequently replaced, which in return contributes to a significant rise in the capital cost. Furthermore, polymeric membranes have the disadvantage that they cannot operate at real and harsh industrial conditions such as high temperatures and pressures. In order to avoid the above critical drawbacks and possibly propose a stable membrane contactor system, the use of novel ceramic hollow fiber membrane contactors for propylene/propane separation while using silver nitrate solution as the absorbent solvent is recommended.

The ceramic hollow fiber membranes were successfully fabricated, modified, characterized, and finally assembled together into a membrane module where propylene/propane separation was carried out under a variety of operating parameters and initial conditions. The modification step was an important factor to ensure that the hollow fiber was hydrophobic to avoid membrane

doi:10.1016/j.proeng.2012.08.522

wetting while in contact with silver nitrate solution. The contact angle of the modified fibers was significantly improved from 33º to 110º as shown below in Fig. 1. The modification of the hollow fibers were further confirmed by breakthrough pressure measurements, as the breakthrough pressure was 1 and 3 bar for unmodified and modified hollow fibers, respectively.

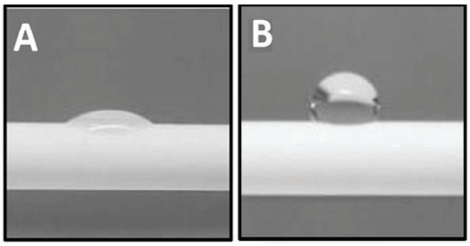

Fig. 1. The contact angle of original (A) and modified (B) ceramic hollow fibers.

The performance of propylene/propane separation was evaluated by the % removal and propylene flux across the membrane for various operating conditions. The effect of operating gas flow and liquid flow rates on the % removal and propylene flux is shown in Fig. 2. The absorption rate of propylene seems to increase with decreasing the gas flow rate and increasing the liquid flow rate which has been extensively reported for similar gas absorption processes using polymeric hollow fiber membrane contactors.

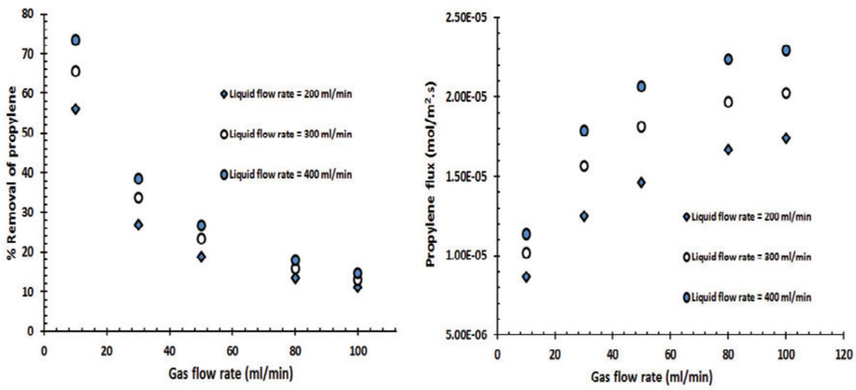

Fig. 2. The % removal and propylene flux for a gas mixture containing 10% C_3H_6 and 90% C_3H_8, while the concentration of AgNO3 was 0.2 M. Operating gas temperatures and pressures were 298 K and 1 bar, respectively.

In the present ceramic hollow fiber system, the overall mass transfer coefficient can be described by considering three resistances in series, i.e., the gas film resistance, membrane resistance and the liquid film resistance [8]. In the case of using modified, hydrophobic membranes, the pores can be assumed to be completely operating in the dry mode where no wetting occurs. The experimental results were analysed using the Wilson plot [9] technique to determine the experimentally mass transfer resistance in the membrane. From the intercept of Fig. 3, the ceramic hollow fibers exhibited a membrane transfer resistance that is lower than 5% of the overall mass transfer resistance in the system.

This performance was compared with PTFE and PVDF membrane modules which are two of the most common commercially available polymeric hollow fiber membranes and also the most studied in the literature among authors [10]. The results show that the ceramic membrane performs as well as the highly hydrophobic PTFE membrane and much better than the PVDF membrane, which could be attributed to partial or complete wetting occurring in the latter.

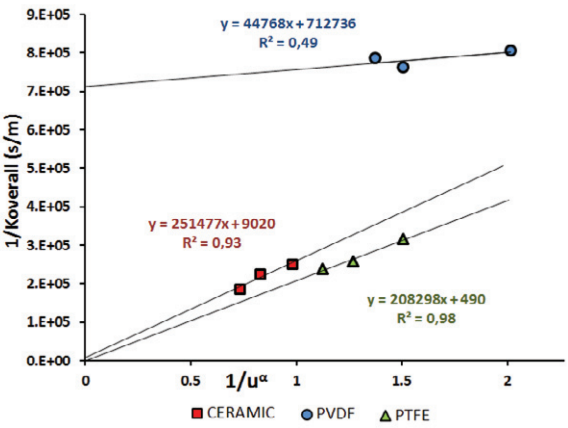

Fig. 3. The overall mass transfer resistance as a function of liquid velocity for ceramic, PVDF, and PTFE hollow fiber membrane contactors.

Although the performance of the PTFE membrane was slightly better than that obtained by the ceramic membranes in the initial stages, it is anticipated that performance of the polymeric membranes may change in the long term due to the chemical incompatibility and thus, deterioration in the separation performance should be observed. Further results on the long term stability would be presented.

References

[1] P.F. Bryan, Removal of propylene from fuel-grade propane. Separation and Purification Reviews 33 (2004) 157.

[2] R.B. Eldridge Olefin/paraffin separation technology: A review. Industrial and Engineering Chemical Research 32 (1993) 2208.

[3] R. Faiz, K. Li. Olefin/paraffin separation using membrane based facilitated transport/chemical absorption techniques. Chemical Engineering Science 73 (2012) 261.

[4] M. Fallanza, A. Ortiz, D. Gorri, I. Ortiz, Improving the mass transfer rate in G–L membrane contactors with ionic liquids as absorption medium. Recovery of propylene. Journal of Membrane Science 385–386 (2011) 217.

[5] K. Nymeijer, T. Visser, W. Brilman, M. Wessling. Analysis of the complexation reaction between Ag+ and ethylene. . Industrial and Engineering Chemical Research 43 (2004) 2627.

[6] D. deMontigny, P. Tontiwachwuthikul, A. Chakma, Comparing the absorp- tion performance of packed columns and membrane contactor. Industrial and Engineering Chemistry Research 44 (2005) 5726.

[7] V.J. Kwasniewski, N. Calamur, M.P. Kamminsky, J.A. Mahoney, C.G. Scouten, R.A. Wilsak, Unsaturated hydrocarbon separation and recovery process. U.S Patent, 5,863,420 (1999).

[8] S. Boributh, S. Assabumrungrat, N. Laosiripojana, R. Jiraratananon, Effect of membrane module arrangement of gas–liquid membrane contacting process on CO2 absorption performance: A modeling study. Journal of Membrane Science 372 (2011) 75.

[9] E. Drioli, A. Criscuoli, E. Curcio, Membrane Contactors: Fundamentals, Applications and Potentialities, Elsevier Science, Amsterdam, (2006).

[10] S.A.M. Marzouk, M.H. Al-Marzouqi, M. Teramoto , N. Abdullatif , Z.M. Ismail, Simultaneous removal of CO_2 and H_2S from pressurized CO_2–H_2S–CH_4 gas mixture using hollow fiber membrane contactors, Separation and purification technology 86 (2012) 88.

Keywords: propane/propylene separation, ceramic hollow fiber, membrane contactor