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Gas–liquid membrane contactor for ethylene/ethane separation by aqueous silver nitrate solution

Nayef Ghasem *, Mohamed Al-Marzouqi, Zahoor Ismail

Department of Chemical & Petroleum Engineering, UAE University, Alain City, United Arab Emirates

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ABSTRACT

Separation of light olefin from paraffin having the same carbon number is one of the most energy intensive separations in petrochemical processes, which uses very long distillation columns with very high number of trays. This is attributed to the very small differences in the relative volatilities. The purpose of this work is to study the absorption performance of a home-made PVDF hollow fiber membrane fabricated using thermally induced phase separation method. Separation of ethylene from an ethylene–ethane gas mixture, using a hollow fiber membrane based absorption–desorption system with aqueous silver nitrate as absorption solvent, and to enhance separation process with a purchased polypropylene hollow fiber membrane module used for stripping purposes. Experiments on the absorption of ethylene from ethylene–ethane mixture, into silver nitrate solutions were performed. The effects of initial ethylene concentration in feed gas, silver nitrate concentration in the inlet solvent, liquid and gas flow rates were investigated. Results reveal that ethylene/ethane separation factor increases with silver nitrate concentration and liquid flow rates. A two dimensional mathematical model was developed for this purpose. Model predictions were validated with experimental data. Model predictions were in good agreement with experimental results.

1. Introduction

Light olefins such as ethylene and propylene are produced in huge quantities in petrochemical plants. Separation of light olefin from paraffin having the same carbon number is one of the most energy intensive separations in petrochemical processes, which uses distillation columns up to 100 m tall and containing over 100 trays due to the very small differences in the relative volatilities and very large reflux ratios and also due to the need for sub-ambient temperatures [1]. These olefins are generally produced by dehydrogenation of the matching alkanes. Their separation is difficult process because of the similarity in molecular sizes and physical properties [2]. Separation of olefin/paraffin is important in the petrochemical industry [3]. Traditional systems, like distillation, other methods such as extractive distillation and absorption are also expensive and consuming energy; studies show that these methods have no improvement over traditional distillation. Recent studies show that membrane separation is an alternative, less-expensive separation method [4–6]. Using gas liquid membrane contactor to separate ethylene from ethane and silver nitrate as carrier solution provide promising results [7,8]. The separation is based on the ability of silver ions to reversibly complexate olefins. A technical and economical evaluation of the separation of propylene and propane using an aqueous silver salt solution as the absorption liquid was previously investigate; results show that using membrane contactor is economically viable process [9]. The conventional distillation drawbacks motivate researcher to develop a substitution separation technology for olefin/paraffin separation. Membrane contactors using silver nitrate for the absorption of olefins from an olefin/paraffin mixture was a talented process [10–14,1,15].

Gas–liquid membrane contactors is outstanding way to carry out gas–liquid separation processes in such a method that membrane contactors have a large area per unit volume, the gas and the liquid flow rate can be controlled independently differing from that frequently used in packed column [16]. Membranes, is an energy competent, environmental friendly, proved to be useful for the separation of olefin/paraffin mixtures. By contrast, Selective polymeric membranes for olefin/paraffin are four to five. To replace or supplement distillation for the separation of olefins and paraffin in steam crackers or propane dehydrogenation plants, membranes with selectivity of 10 or more are needed [17].

The technology was industrially investigated on the a stream from a polypropylene plant using commercial scale hollow fiber

* Corresponding author. Tel.: +971 3 713 5313; fax: +971 3 713 4962.
E-mail address: nayef@uaeu.ac.ae (N. Ghasem).

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Nomenclature

$C_{g,in}$	inlet gas concentration (mol/m^3)
$C_{g,out}$	outlet gas concentration (mol/m^3)
C_i	concentration of component i; 1: C_2H_4, 2: C_2H_6, 3: $AgNO_3$ 4: $Ag{\cdot}C_2H_4$ (mol/m^3)
$C_{i,Memb}$	concentration of component i in the membrane section (mol/m^3)
$C_{i,shell}$	concentration of component i in the shell section (mol/m^3)
$C_{i,tube}$	concentration of component i in the tube section (mol/m^3)
D_i	diffusion coefficient of component i
d_{in}	inner diameter of hollow fiber diameter (m)
d_o	outer diameter of hollow fiber diameter (m)
H	Henry's constant
k_c	equilibrium rate constant (m^3 mol^{-1})
k_1	forward reaction rate constant (m^3 mol^{-1} s^{-1})
k_2	reverse reaction rate constant (s^{-1})
L	length of hollow fiber membrane (m)
m_i	physical solubility of component i
Mw	molecular weight of gas (g mol^{-1})
p	pressure (Pa)
Q_g	inlet gas flow rate (m^3 s^{-1})
Q_L	inlet liquid flow rate (m^3 s^{-1})
R_g	universal gas constant (8.314 J mol^{-1} K^{-1})
r_1	inner tube radius (m)
r_2	outer tube radius (m)
R	inner shell radius (m)
T	absolute temperature (K)
V_z	velocity of fluid inside the module in z-direction (m s^{-1})
V_{max}	maximum velocity (m s^{-1})
z	axial distance (m)

Greek letters

ρ	polymer density (g cm^{-3})
φ	membrane void fraction
ε	membrane porosity (–)
τ	tortuosity

modules saturated with silver nitrate ($AgNO_3$) solution. Liquid hexane was used to sweep the leaked solvent from the fibers; membrane deactivation due to water loss was shown to adversely affect fiber performance. Lack of tolerance to poisons such as H_2S and acetylenes was also acknowledged as a process deficiency. A similar supported liquid membrane contactor module using a recirculation silver nitrate solution was used [18]. The process could achieve separation but not to the extent of commercial success because of high cost and the carrier solution was unstable. Different olefin complexing carriers in the hope of identifying a more stable carrier for facilitated transport membranes were studied in literature. The most commonly considered carriers other than silver are copper salts was copper (I) ions form π-bond complexes with olefins in the same manner that silver does. Copper carriers also suffer from stability problems [19]. Alternate carriers that functions via a different complexing mechanism have been examined such carrier is molybdenum sulfide dimmers that reversibly complex olefins and are unaffected by H_2S. Reversible olefin complexation for a palladium-containing cubane compound was reported in literature [20]. Experimental investigation reveals that these materials are stable in the presence of hydrogen and acetylenes, but degrade upon contact with H_2S or oxygen. Membrane was used as an air-sweep vacuum membrane distillation using fine silicon, rubber, hollow-fiber membranes [21]. Separation of olefin from olefin/paraffin with other techniques was studied [22–26]. Results reveal that carrier concentration and trans-membrane pressure has significant on separation factor. Gas permeability of combined membrane systems with mobile liquid carrier were studied by Shalygin et al. [27]. System permeability for individual gases (CO_2, O_2, and H_2) and its dependence on a flow rate of a liquid phase were studied. Two theoretical models were developed: the model of gas transfer through a selective membrane valve system with a mobile liquid absorbent and the model of a non-steady-state transfer of CO_2 through the immobile layer of aqueous potassium carbonate solution.

In the present work the effect of ethylene initial feed concentration, silver nitrate concentration and inlet gas flow rate on the separation factor of ethylene/ethane mixture using polymeric hollow fiber membrane contactor module and silver nitrate carrier was experimentally investigated.

2. Experimental work

2.1. Reagents and materials

Silver nitrate, purchased from Sigma Aldrich, Germany, was used as a stripping solvent. Silver nitrate aqueous solutions were prepared using distilled water. Ethylene (99.95%) and Ethane (99.5%) gas cylinders were purchased from Air Products, UAE. Nitrogen (99.99%) gas cylinder was purchased from Sharjah Oxygen (UAE).

2.2. Experimental

The experimental setup used in the ethylene–ethane separation is shown in Fig. 1. The separation process consisted of absorption and desorption hollow fiber membrane modules. A feed gas stream of different flow rates of ethylene and ethane gas mixtures were prepared using mass flow controllers (Alicat Scientific) and fed to the shell-side of the absorption HFM module. The gas composition was determined using (Ethylene gas analyzer, X-Stream XE, Emerson), $CaSO_4$ drying agent was used to dry the gas stream to avoid condensation inside the analyzer. An 8-CH ADC data logger (Pico Tech, UK) was used for data monitoring. The silver nitrate aqueous solution was pumped to the tube-sides of the absorption and desorption modules; inlet flow rates of the aqueous silver nitrate solution was adjusted by using peristaltic pump (Masterflex). A sweep gas; nitrogen was used at the shell-side of the desorption module. The flow of the nitrogen stream was regulated using a flow meter. All experiments were performed at room temperature 25 °C, and under atmospheric pressure.

The home-made 28% PVDF hollow fiber membrane modules were fabricated via thermally induced phase separation method [28]. The SEM images (cross section, inner and outer surface) of fabricated polymeric (28% PVDF/72% triacetin) hollow fiber membrane are shown in Fig. 2. The membrane shows spherulites type of structure. The properties of the fabricated hollow fiber membranes are shown in Table 1.

The commercially polypropylene module (MiniModule® 1.0 × 5.5 part # G543, Membrana, Charlotte, N.C., USA) is employed for stripping purposes only. The module consisted of 2300