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Polymeric membranes for light olefin/paraffin separation

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ABSTRACT

Olefins are produced in the petrochemical industry by steam cracking of parrafins, followed by repeated compression and distillation to separate the complex vapour mixtures. The second step is considered to be a highly energy-intensive process and have been extensively studied for possible replacements. The use of membranes has been the focal point of research as a new means of olefin/paraffin separation due to its lower operating and capital costs. In this article, a comprehensive review is presented for the application of polymeric membranes in light olefin/paraffin separation. It covers all types of membrane materials starting from the conventional polymers to more advanced ones such as polyimide and copolyimide membranes. Permeation and separation characteristics of all polymeric membranes are summarized and discussed in great details.

1. Introduction

1.1. Importance of olefins

Light olefins such as ethylene and propylene are very important to petrochemical industries because they are utilized as main building blocks for many essential chemicals and products for industrial and domestic consumptions. Approximately, 80% of ethylene produced in the United States and Europe is used to create ethylene oxide, ethylene dichloride, and polyethylene. Ethylene oxide is a key raw material in the production of surfactants, detergents, and automotive anti freeze solutions. On the other hand, propylene is a raw material for a wide variety of products including polypropylene, which is considered as a versatile polymer used in packaging and other important applications such as textiles, laboratory equipment, and automotive components. Propylene is the second highest volume petrochemical feedstock after ethylene. Global propylene demand during 2007 saw a growth rate estimated at 5.5% bringing total propylene consumptions up to about 45.1 million metric tons, which led to turnover of about 65 billion US dollars [1]. The 5-year outlook shows world propylene demand growth to average slightly less than 5% per year [2]. The production of polymers and other special chemicals from mono-olefins such as propylene requires the olefin to be of extremely high purity (>99.9%), and since light olefins are commonly produced together with paraffin hydrocarbons, i.e. ethane and propane, the techniques for separating both hydrocarbons are of primary importance to the petrochemical industry [3]. Additionally, a significant amount of the light olefins produced during the refining of crude oil is used as refinery fuel and therefore, are considered too valuable to be burned as secondary components.

1.2. Current separation techniques

For nearly seven decades, separation of olefins such as ethylene and propylene from refinery catalytic cracker off-gases and effluent streams have been performed by a highly energy-intensive cryogenic distillation in a single or double column process with 150–200 trays at temperatures between 233 and 183 K and pressures ranging from 16 to 20 bar. The reason for the low temperatures and high pressures operating conditions in such distillations is the similar boiling points of olefins and their respective paraffins. The separation process is considered to be highly heat integrated with typical ethylene/propylene refrigeration systems used for low-temperature cooling [3]. These systems are expensive to build and operate, and are only economically attractive for streams containing high quantities of olefin, such as those from large refinery catalytic crackers. As mentioned by Eldridge [3], the U.S. Department of Energy estimated 0.12 Quads (1 Quad $= 10^{15}$ BTU) of energy was used annually for cryogenic distillation of olefin/paraffin mixtures. Furthermore, a large portion of the capital cost of a typical cryogenic plant was devoted to the large distillation columns in the separation chain units.

1.3. Alternative technologies

The high level of heat incorporation and enormous capital cost in cryogenic distillation necessitates the need for alternative separation technologies to be considered to replace the current technologies. Several attempts have been made with extractive distillation processes. In those schemes, a high-boiling polar compound is needed where it

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enters the column above the feed introduction point. Krupp-Koppers [4] implemented extractive distillation for 2-butene/*n*-butane separation where a mixture of morpholine derivatives was used as the solvent. An olefin recovery of 99% was achieved from a vapour mixture containing 48 wt.% of *n*-butane. The application of extractive distillation was also used by Kumar et al. [5] for propylene/propane separation. Detailed cost calculations were performed for an optimized extractive distillation scheme with a hypothetical solvent. The thermodynamic characteristics of the solvent had a major impact on the process economics, and based on the computer simulations results by Kumar et al. [5], it was concluded that extractive distillation offers no advantage over traditional distillation.

Other processes such as the use of molecular sieves for olefin/paraffin separations have been also investigated for several decades [6,7]. Studies with 13X molecular sieves indicated that propane and propylene can be separated using an equilibrium adsorption step followed by a stepwise thermal regeneration variable-temperature stepwise desorption (VTSD) [6]. Experimental and modeling results indicated that this approach was feasible for binary gas mixtures containing less than 25 mol% propylene [6]. This disadvantage makes the process less attractive for industrial applications which may contain high concentrations of propylene. Additional data for the VTSD process was presented by Kulvaranon et al. [7]. Experimental results were given for propylene/propane separation using 5A and 13X molecular sieves. An economic comparison indicated that the VTSD energy costs were lower, but capital costs were higher than a comparable distillation process [3]. Recently, Grande et al. [8] studied the selective adsorption of propylene from gas mixtures containing propane with lithium ion exchanged zeolite 13X. The difference in loading between both gases became larger for lithium exchanged zeolites than ordinary 13X sodium zeolites. Due to the isotherm steepness as well as the large heat of adsorption, Grande et al. [8] concluded that this adsorbent was not suitable for vacuum pressure swing adsorption (VPSA) applications but might be attractive for thermal swing adsorption (TSA) applications. An alternative option would also be the removal of traces of propane or/and propylene from air.

Ethylene/ethane separation using ion-exchanged molecular sieves have also been investigated by Schoellner et al. [9] who used ion exchanged zeolites with K, Ba, and Mg ions for ethylene/ethane separation. Ethylene loadings per 100 g of these adsorbents were only in the range of 3.8–5.4 g. Although using adsorption techniques for olefin/paraffin separation showed low loadings of olefins, and thus makes the process less attractive for industrial applications, the use of ion-exchanged molecular sieves for olefin/paraffin separation is still showing in today's literature. Recently, Shi et al. [10] demonstrated the application of Na–ETS-10 molecular sieves for the separation of ethylene/ethane gas mixture obtained from an industrial process stream (59% C_2H_4, 41% C_2H_6). In a laboratory-scale demonstration, both high purity ethane and significantly enriched ethylene were produced, while the regeneration of the Na–ETS-10 adsorbent for further separation cycles was possible by both steam and microwave desorption. Anson et al. [11,12] also used ion exchanged molecular sieves for ethylene/ethane separation. In their approach, ethylene and ethane were separated by inverse-phase gas chromatographic and gravimetric isotherm techniques on ion-exchanged forms of ETS-4 and RPZ titanosilicate molecular sieves. Gas chromatography results revealed that kinetic separation of ethylene from ethane was possible using ETS-4 and RPZ adsorbents exchanged with Zn and mixed Ca/H. Due to the molecular sieving character of the ETS-4 and RPZ adsorbents, steric effects were observed for the adsorption of ethylene and ethane, and it was concluded that the contact time between the adsorbent and the gas mixture was the key factor in the separation of these gases. Anson et al. [11] suggested that ETS-4 and RPZ materials exchanged with Zn or Ca/H were excellent candidates for the commercial adsorptive separation of ethylene and ethane.

Nevertheless, the techniques and separation methods for olefins and paraffins gas mixtures certainly create a great potential for lowering capital, operating, and energy costs if more economical methods are investigated and implemented. However, they are currently very few non-distillation processes being used in the chemical industry due to the inherent problems associated with these alternative processes [3]. Before getting into specific purposes of this review article, the review work performed by Eldridge [3] is first acknowledged. The review article tackled the traditional and nontraditional technologies for the separation of light olefins and paraffins. The addressed technologies ranged from conventional low-temperature distillation to chemical complexation using copper and silver ions. The advantages and disadvantages of these systems were well presented and summarized.

1.4. Membranes potential for olefin/paraffin separation

Membrane technologies clearly present itself as an attractive alternative to reduce the large capital and operating costs of the current cryogenic distillation for olefin/paraffin separation. Typically, membrane systems show a 4 fold decrease in operating cost compared to distillation units. It is therefore not surprising that an enormous quantity of reports have been published on olefin/paraffin separation using membrane technologies. According to a recent survey by Semenova [13] there are over 2000 articles that have been published on the use of membranes for hydrocarbon separations and removals over the span of the last 30 years. However, the share of patents within these articles is about one-third only [13], which shows that researchers are still looking into the enhancement of the available membrane systems/processes for olefin/paraffin separation before possible commercialization. These membrane techniques can be categorized into three main groups, that is, polymeric, inorganic, and facilitated transport membranes.

The use of polymeric membranes without a carrier for olefin/paraffin separation has been studied rather extensively. These membranes include various materials such as glassy, cellulosic, and rubbery polymers. The permeation and separation characteristics of these membranes are governed by both the molecules and polymers properties such as molecule size and shape; and polymer structure, packing, and rigidity, respectively. Among these materials, glassy polymers have been studied intensively for olefin/paraffin separation as well as the separation of aromatic, alicyclic, and aliphatic hydrocarbons, whereas rubbery polymers were mainly used in gas/vapour separation applications such as hydrocarbon separation from air mixtures, as well as pervaporation processes such as hydrocarbon extraction from their aqueous solutions. Semenova [13] provides great discussions and analysis about these applications for both glassy and rubbery membranes.

On the other hand, carbon molecular sieves (CMS) membranes showed promising olefin/paraffin separation compared with ordinary polymeric membranes. These membranes are usually prepared by the pyrolysis of polymeric precursors for which polyimide materials have been frequently used [14–16]. CMS composite membranes composed of a selective carbonized layer on top of an inorganic support seems to have excellent mechanical strength but suffers from complicated preparation procedures. Conversely, inorganic hollow fiber membranes [17–19] offer simple preparation procedures, but have very poor mechanical strength which makes it very difficult to scale up. Nevertheless, the development of CMS and inorganic membranes for olefin/paraffin separation is rather new and yet to be studied intensively.

The last and most important type of membranes for olefin/paraffin separation is facilitated transport membranes. It is well known that olefins are capable of forming reversible chemical bonds with transition metal ions due to the specific interaction between the olefin's hybrid molecular orbitals and the metal's atomic orbitals, commonly known as the π-bonding. This chemical complexation offers a great advantage that the bonds formed between transition metal ions and olefins are stronger than those formed by Van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bounded. At the same time, the bonds are