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Perspectives, development and applications of membrane-liquid contacting systems for gas and vapour separations

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1. Introduction

An important area of membrane technology which is of continuing interest concerns improvements in the productivities and selectivities of gas-separation systems. This can be achieved in various ways. Certain improvements can be obtained by combining a second, but conventional separation operation with membrane technology, to create an integrated membrane hybrid process (IMHP). IMHP is a general term for various process configurations, formed, for example, when highly selective affinity interactions and high-throughput membrane separations are combined. In such a case the synergy of various separation processes is achievable in one integrated system. An excellent example of the efficiency of a "contacting membrane system with flowing-liquid carriers" for mass transfer is the transport of dioxygen by hemoglobin in all mammals. The human lungs for example have a "contacting" surface area which is 30-50 times greater than the external surface area of the body.

One of the obvious disadvantages of such artificial systems is the complexity of the entire system, compared to those of conventional membrane separation. The complexity arises from difficulties in maintaining high liquid fluxes and the need for additional liquid pumps, etc. It is for these reasons that the need to optimize contacting systems (which includes: selection of an appropriate membrane, liquid carrier, membrane module configuration, mode of operation, etc.), is one of the most important aspects in the development of competitive membrane contacting systems.

The main focus on aspects and problems connected with the optimization of processes taking place in a nonporous polymeric membrane contacting system with a flowing liquid (membrane-liquid contactors) is given in this paper.

In this paper, the abovementioned problems are discussed in relation to the separation of olefins from paraffins, the oxygenation and deoxygenation of water, and the selective separation of air by means of a membrane contacting system. Various physicochemical questions relating to membrane contactors are discussed. These include the problems of chemical complexation in flowing-liquid membranes and mass-transfer phenomena. Schemes for organization of the process (module design, mode of operation, etc.) are also suggested and discussed.

To analyze the results of separation experiments, a theory which was developed for permeation in laminated membranes, for the case when one of the layers is a liquid and this liquid is able to move (flow), was adapted. The details of the resulting mathematical derivation are given. This paper also contains computer simulation of an ethylene/ethane separation process in a liquid-membrane contactor and its comparison with experimental results.

2. Experimental

2.1. Olefin/paraffin separation

Several questions regarding the use of nonporous polymeric membranes in membrane contactors remain unanswered, however, for example, the stability of such a system; the possibility of separating higher liquid olefins from paraffins, and the mathematical description of separation processes in membrane contactors (MC).

Figure 1 shows the principle of liquid olefin/paraffin separation by means of a membrane contactor with non-porous membranes in the range of up to C_{10}. Silver nitrate/ethylene glycol solutions were used as a "selective" carrier for liquid olefins. The same principle of operation was used for the separation of gaseous mixtures of olefins and paraffins (Bessarabov et al., 1995).

Figure 2 shows the trend of the solubility (uptake rate, mol/L) of unsaturated liquid hydrocarbons in ethylene glycol/silver nitrate solutions of various concentrations, (mol/L). The diagram is based on the experimental results on hydrocarbon solubilities measured at 23 °C.

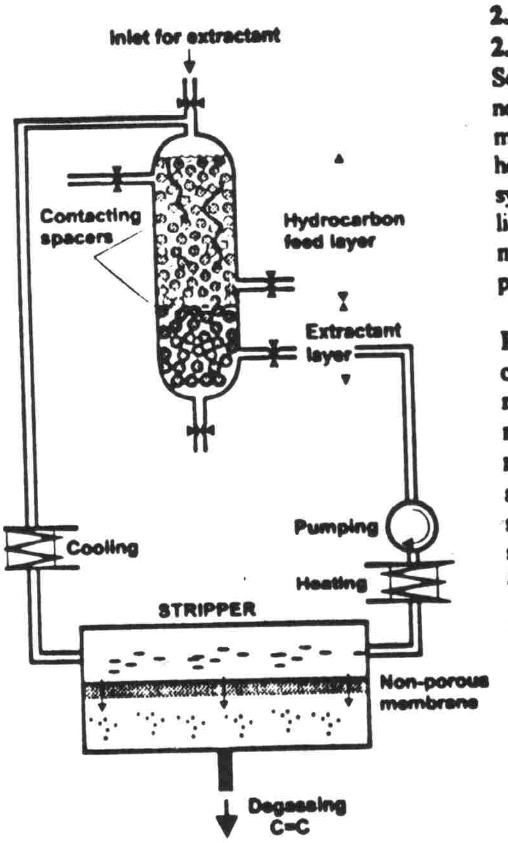

Figure 1. *Schematic diagram of a hybrid membrane/extraction system for olefin/paraffin separation.*

2.2. Air separation for the production of an oxygen-enriched gas stream. The purpose of this study was to demonstrate the possible application of the membrane contacting system for the separation and purification of oxygen from air. The operating principle of the membrane contacting system is analogous to that used for olefin/paraffin separation.

Cobalt(II)-based compounds can be used as a "carrier" for oxygen since a wide range of cobalt(II) compounds form molecular oxygen complexes. Such compounds differ widely in chemical composition, spin state of cobalt(II), solvent media, etc. Schiff bases are macrocyclic compounds that are formed by the Schiff base condensation reaction. In general, a reversible reaction of dioxygen binding by such compounds can be represented as the following:

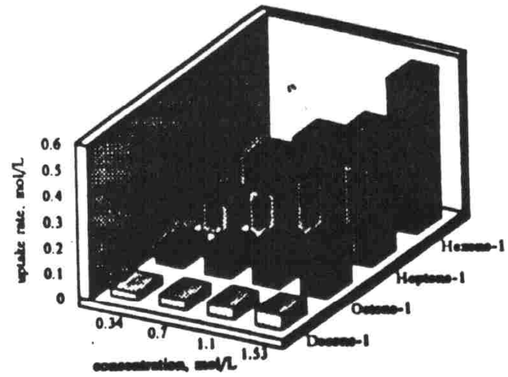

Figure 2. *Solubility (mol/L) of hydrocarbons in ethylene glycol/silver nitrate solutions (mol/L), based on experimental data.*

$$n[\text{cobalt(II)-Ligand}] + O_2(\text{gas}) \Leftrightarrow$$
$$\Leftrightarrow [n(\text{cobalt(II)-Ligand})\text{-}O_2]$$

A complex of Co(II) with *α-α'-dipyridyl* and the additional base *gramine* was used as a carrier for oxygen.. Distilled DMFA (dimethylformamide) was used as a solvent. Asymmetric nonporous PVTMS membranes were used as the barrier between gas and liquid phases in the membrane contactor.

3. Results and discussion

3.1. Olefin/paraffin separations. The separation of binary mixtures was carried out. For example, the 1-hexene/n-hexane separation factor ranged between 40 and 70. The flux of 1-hexene was up to 1.4×10^{-6} g/sec.cm^2 at 62°C. The abovementioned data were obtained with PDMS-based membranes.

3.2. Air separation. Oxygen-enriched air with up to 70% (vol) oxygen was obtained in the membrane desorber (stripper). It was found that the oxygen carrier was very unstable. It was oxidized by oxygen in a few hours. Fast degradation of the carrier was explained by the further side reactions leading to reduction of dioxygen to H_2O and to the oxidizing of a chelating ligand, for example:

$[\text{Co-Ligand}] + O_2 \Leftrightarrow [\text{Co-Ligand-}O_2]^-$
$[\text{Co-Ligand-}O_2]^- + [\text{Co-Ligand}] \Leftrightarrow [\text{Co-Ligand-}O_2\text{-Co-Ligand}]^{2-}$
$[\text{Co-Ligand-}O_2\text{-Co-Ligand}]^{2-} \Leftrightarrow 2[\text{Co-Ligand-O}]^-$
$[\text{Co-Ligand-O}]^- + [\text{Co-Ligand}] \Leftrightarrow [\text{Co-Ligand-O-Co-Ligand}]^{2-}$

4. References

D.G. Bessarabov, R.D. Sanderson, E.P. Jacobs and I.N. Beckman, *Ind.Eng.Chem.Res.*, 1995, 34, 1769-1778