Organic Separations with Membranes

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Introduction

This paper presents an overview of present and emerging applications of membrane technology for the separation and purification of organic materials. This technology is highly relevant for programs aimed at minimizing waste in processing and in the treatment of gaseous and liquid effluents. Application of membranes for organic separation is growing rapidly in the petrochemical industry to simplify processing and in the treatment of effluents, and it is expected that this technology will be useful in numerous other industries including the processing of nuclear waste materials.

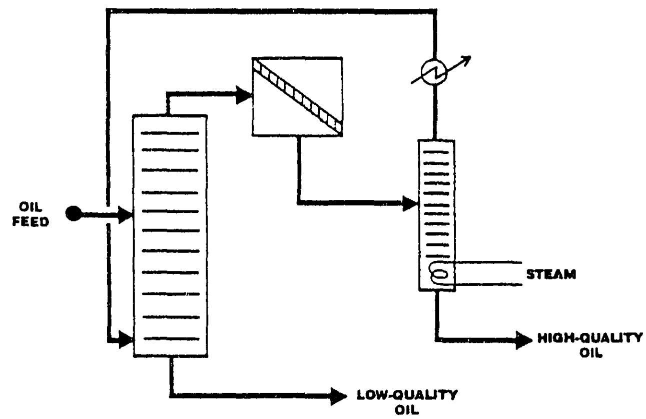

Figure 1. Allied-Signal Process for Solvent Recovery

Commercial Applications

There are four major areas where membranes are being used to treat organics. First, membranes are being used to remove acid gases (CO_2, H_2S) from methane. The major application is in natural gas production, but could also find application for other gas streams which must be treated before being released into the environment.

The second emerging commercial use is in the recovery of solvents from mixtures of solvents with chemical products. The technique may find wide application in industries beyond petrochemicals, and in particular, can form part of systems for environmental management. An example would be the coupling of membranes for solvent recovery with solvent extraction.

In our laboratory (Kulkarni et al. 1986; Funk et al. 1986), we have developed membranes for the recovery of solvents from heavy oil as illustrated in Figure 1. Petroleum deasphalting typically uses large ratios of light paraffins (propane to pentane) and thus is an ideal application for solvent recovery via membranes. It is interesting that this separation is by ultrafiltration with the size selectivity due to both the porous membrane and the surface layer formed on the membrane. Figure 2 shows the long-term performance for a spiral-wound module of polysulfone processing a mixture of Arabian Heavy Vacuum Resid with pentane as the solvent. The separation capability is moderate, but the membrane and module components were not degraded by the organic components.

These studies are with polysulfone-based membranes which are stable to the heavy oil and paraffinic solvents (but not to light aromatics which are not present in these feed streams). The number of polymeric materials for use in organic separations is not large since most tend to swell or dissolve. Examples of candidate materials are aromatic polyamides, polyvinylidene fluoride, polytetrafluoroethylene, and polyamides.

The third commercial area is pervaporation and this is rapidly becoming established technology in Europe for the dehydration of alcohols. This technique is potentially valuable for environmental systems as a way to efficiently remove organics from waste streams. It may also be

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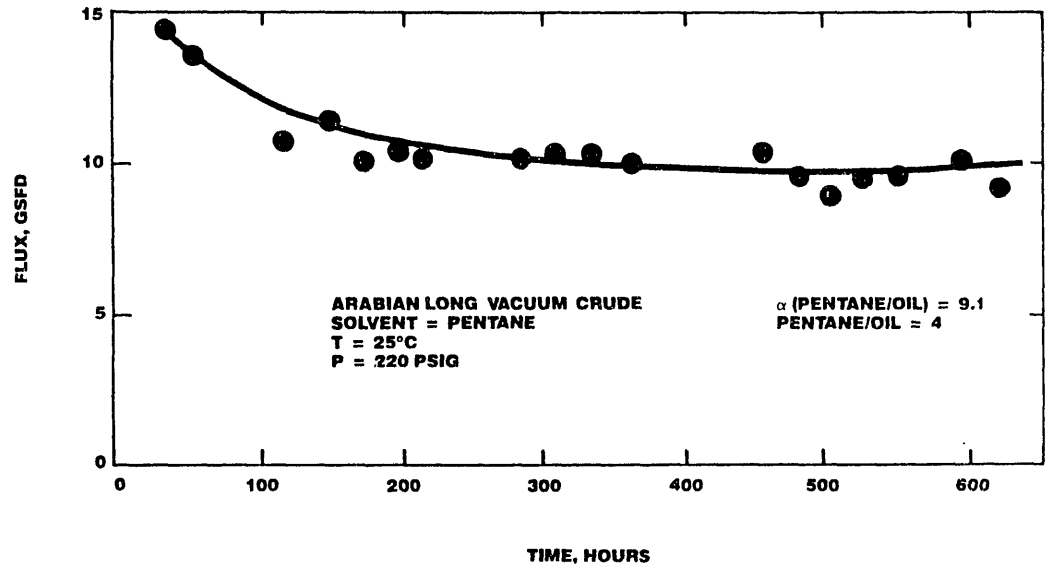

Figure 2. Long-Term Performance of Module for Solvent Recovery

combined with other separations such as air stripping, adsorption, and solvent extraction.

The fourth area of growing commercial viability is solvent vapor recovery and is also centered in Europe, although much of the underlying science of how rubbery membranes such as silicone separate light organic gases from air was done in the United States. The separation factors are enormous (trichloromethane/N_2) > 1000 and the membranes are both inexpensive and easy to fabricate. At the 1990 International Congress on Membranes, it was impressive to see pictures of a large-scale unit operating in Germany. A serious engineering commitment had been made to scale up the process.

Frontiers of Research

There are two frontier areas involving organic separations which are highly relevant for the development of separation systems for environmental management.

First, there are some fascinating new hybrid systems being proposed that effectively integrate membranes with other separation processes. Rautenbach and Albrecht (1985) have proposed a combination of pervaporation with extractive distillation for the separation of benzene/cyclohexane mixtures. The group at Air Products and Chemicals (Choe, Agrawal et al. 1990) presented an interesting system concept on the combination of membranes with adsorption: one application is the recovery of H_2 from a gas mixture. Union Carbide is also exploring synergy of this type of process (Doshi 1987; 1988). Professor Stern at Syracuse University (Acharya and Stern 1988) has been exploring liquid organics (e.g., benzene/cycloexane) separation with a variation of pervaporation where on the permeate side of the membrane there is a liquid phase instead of low pressure.

Second, membrane technology is being explored in studies which combine membrane separations with chemical reactor technology. There are three major conceptual advantages: (1) reaction, concentration, and separation can be integrated into a single process; (2) the system can be operated to enhance thermodynamically limited or product-inhibited reactions; and (3) reaction rates can be controlled to give very selective reactions.

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