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Development of large-scale applications in organic solvent nanofiltration and pervaporation for chemical and refining processes

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Abstract

New membrane, modules, and systems are under development for large-scale organic/organic separations. Practical applications are envisioned in the refining, chemical, pharmaceutical, and polymer industries. A large-scale organic solvent nanofiltration (OSN) process is MAX-DEWAX^{TM} for solvent recovery in lube dewaxing. A commercial installation has been in operation since 1998 at a feed rate of 5800 m^3/day (36,000 barrels/day). A pervaporation process, S-Brane^{TM}, is also available for comparable large-scale operations. S-Brane selectively removes sulfur containing hydrocarbon molecules from fluidized catalytic cracking (FCC) and other naphtha streams. A 300 barrels/day demonstration plant has been run on-stream using FCC light and intermediate cat naphthas. S-Brane reduces the overall capital and operating cost for clean fuel compliance, and also provides a means for preserving octane value in hydrotreating based technology.

There are several key steps in the development of a robust membrane process that can be moved from lab-scale to pilot plant trials to a demonstration unit on-line at a refinery. These steps expand in complexity and size as process development moves forward. Both MAX-DEWAX and S-Brane are presented as examples of applications that have moved through this progression. Since these processes are large-scale and relatively low capital cost compared to conventional technologies, gains in yield, quality, or energy savings are found to offer significant economic benefits.

Experimentally, it appears that high-pressure nanofiltration and low-pressure pervaporation are governed by the principles found in solution-diffusion models. Data taken in OSN mode is used to estimate pervaporation performance. Choice of membrane operating systems is dependent on the composition of the feed stream and the required product quality. In some cases, the high throughput for OSN outweighs the higher selectivities gained in pervaporation, since OSN is inherently a lower cost process to operate.

Further investigations of new applications include toluene recovery from a toluene disproportionation unit, lowering benzene levels in gasoline feedstocks to <1%, and integration of membrane separation with aromatics reformer or distillation operations.

Keywords: Process economics; Solvent resistant nanofiltration; Extended tests; Industrial development; Commercial trials

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1. Introduction

Traditional applications for industrial membrane separations in liquid systems have been in a water environment. Membrane systems are now available that can function in organic solvents, opening up new opportunities in the chemical and refining industries. As with reverse osmosis these solvent resistant membranes operate on the molecular scale giving separations in the nanofiltration range. The first large-scale application of this technology was in solvent recovery from the dewaxing operation in lubes processing [1,2].

The refining industry is both energy and separations intensive, suggesting that application of large-scale membrane systems can provide significant benefits. The solvent recovery process in dewaxing is large-scale, handling 5800 m^3/day (36,000 barrels/day) of feed, and provides payback in energy savings, product quality, and increased throughput. The key to successful operation of this membrane system was the integration with the existing process units, and demonstration that membrane operations can show long-term durability in these solvent environments. Both organic solvent nanofiltration (OSN) [3,4] and pervaporation [5] need to be considered in developing other new large-scale applications.

Applications for OSN have been under pilot plant trial or demonstrated in laboratory experiments in solvent deoiling [6], homogeneous catalyst recovery [7], separation of phase-transfer

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agents [8], and solvent exchange [9]. Exxon Research and Engineering patent literature reports a variety of organic/organic membrane separations including reverse osmosis to recover extraction solvents [10], and separation of alkylaromatics from an alkylation process with aromatics [11].

A distinction can be made between aqueous nanofiltration (NF) and OSN. Water treatment systems use NF to define separation between charged ions and other compounds in aqueous phase, while OSN looks at separations in organic/organic matrixes. A membrane industrially used for aqueous NF is often unsuitable in solvent intensive systems. One reason is that many of the NF membrane substrates are based on polysulfone, which has limited solvent resistance. If the polysulfone or any other substrate collapses upon solvent exposure, the membrane separation will likely fail.

Other potential refining applications are benefited by operating in pervaporation mode. In one pervaporation application, we have focused on removal of organic sulfur compounds from naphtha [12,13] in order to provide clean feedstocks for the gasoline pool. The naphthas from FCC streams are critical in setting sulfur levels in consumer gasoline. Federal regulations are stipulating a sulfur level below 30 ppm S, creating interest in technologies that help achieve this goal. This is another example where a membrane separation is integrated with other process units to improve the performance of the unit as a whole.

A potential industrial pervaporation application is separation of benzene from cyclohexane [14]. Exxon Research and Engineering has explored using pervaporation to separate aromatics from non-aromatics in heavy cat naphtha [15], and reducing the aromatics content of distillate with pervaporation [16]. Jonquières et al. [17] have supplied a recent listing and analysis of patent literature on pervaporation.

Current and proposed refinery applications for membranes are mostly based on polymeric membranes, which can interact strongly with solvents [18]. The nuances of solvent–polymer interactions remain under ongoing investigation. Long-term reactions of a polymer structure to stress of pressure and temperature while in a solvent system are difficult to estimate. This is combined with membrane structures that are not well defined on the small molecular scale, where small structural changes can have large impact on performance. Since refining applications require year-round operations, physical testing of membrane systems for any new proposed large-scale application is currently required in practice. This testing should not be limited to the membrane, but include the module design into which the membrane is fabricated, and how these modules are deployed in an engineered system.

Modeling efforts for OSN have floated between pore-flow, empirical, and solution-diffusion equations [19–24]. Recent refinements of solution-diffusion models have included Peeva et al. [25] using activities to address non-ideal systems, and Wijmans [26] inserting molar volume correction factors into the equations. Paul [27] has updated earlier work from 1975 [20] and shows that limiting fluxes are the same in pervaporation when vacuum = 0 or in hydraulic permeation when applied pressure goes to infinity. Given the dynamic interaction between solvents, solutes, and the polymeric matrix of the active separation layers of membranes, solution-diffusion equations are used in this current work to connect OSN and pervaporation.

In this paper, we review the steps required to develop both OSN and pervaporation systems for high volume refining applications. A theoretical connection between OSN and pervaporation is found to be a useful concept. Rules-of-thumb for selecting the mode of operation are also discussed.

2. Developing a large-scale membrane separation

In developing an experimental membrane system for new refining applications, some key steps are:

- Defining the separation of interest.
- Setting targets for membrane performance.
- Identifying a membrane that can perform the separation (proof-of-concept).
- Demonstrating the separation.
- Testing the membrane in a module design through pilot-plant trials.
- Showing stable long-term operations (time-intensive step).
- Designing a commercial application.
- Building a commercial system.
- Start-up.

Moving from laboratory experiment to pilot plant operations to a demonstration unit becomes progressively more complicated. Fig. 1 illustrates the size scale-up involved in working through these steps. Each step brings an increase in membrane area requirement, equipment, quantity of required feedstocks, time for execution, analytical facilities, technical issues, and operating personnel. These issues are certainly not limited to membrane process development, and had to be addressed in past decades in development of gas separations and reverse osmosis, also molecular-scale membrane separations.

The steps taken in the exploration of S-Brane will be used as an example of this process development. S-Brane treats naphthas to help generate clean fuels. The sulfur content in FCC naphthas consists of aromatic and non-aromatic sulfur containing compounds. Typical structures of these compounds are shown

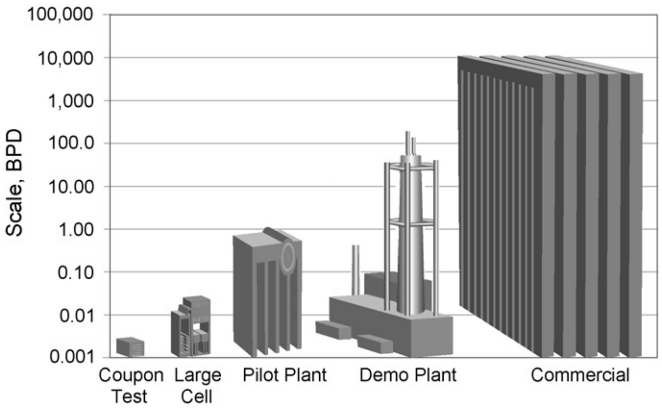

Fig. 1. Pictorial of steps in process development for new large-scale applications. BPD is barrels per day.