Invited Lectures 1

MEMBRANE-BASED GAS AND VAPOR SEPARATIONS

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EXTENDED ABSTRACT

Industrial gas separation by membranes began in 1980 with the introduction of hollow-fiber polysulfone membrane systems by Permea, at that time a division of Monsanto. This first application was the recovery of hydrogen from ammonia reactor purge gas and was soon followed by the generation of nitrogen from air. Today, membrane gas separation ranks second behind cryogenic distillation in terms of nitrogen production, and this application has drawn the industrial gas companies into the membrane field. All major gas companies, except BOC and Linde, now have their own membrane subsidiaries: Air Liquide (Medal, started as a joint venture with Du Pont), Air Products and Chemicals (Permea, acquired from Monsanto), Praxair (Innovative Membrane Systems, acquired from Albany International) and MG Industries (Generon, acquired from Dow).

Other membrane gas and vapor separation applications developed in the 1980s and 1990s are the removal of carbon dioxide from natural gas (Cynara, UOP, Kvaerner, Medal, Permea, Praxair andUBE), the separation of organic vapors from air or nitrogen (MTR, GKSS licensees), the dehydration of organic vapors (GFT, now part of Sulzer ChemTech) and the dehydration of air (Hankison, Parker-Hannifin). More recently the vapor dehydration application (primarily the drying of isopropanol) has seen the introduction of inorganic zeolite membranes by Smart Chemical Company and Mitsui.

Table 1 provides a breakdown of the membrane gas and vapor separation market with sales estimates for the year 2000 as well as sales predictions for the years 2010 and 2020. The current gas and vapor separation market is estimated at $160 million, and overall the market is expected to grow at an annual rate of 8% to $730 million in the year 2020. The market segments expected to grow more rapidly than the average rate are: hydrogen/vapor, natural gas liquids (NGL) from natural gas, vapor/gas and vapor/vapor. This implies that significant expansion of membrane technology will occur in the petrochemical, refining and natural gas industries.

Table 1. Sales estimates and sales predictions for the principal gas and vapor separation applications. Ion conducting membranes, which transport oxygen and are being developed for synthesis gas production, are not included.
NGL: Natural gas liquids (C_{3+})

Application	Annual Membrane System Sales (U.S. $ million)		
	Year 2000	Year 2010	Year 2020
Nitrogen from Air	75	100	125
Oxygen from Air	< 1	10	30
Hydrogen			
H_2/Gas (CO, N_2, C_1, C_2)	25	40	80
H_2/Vapor (C_{3+}, CO_2)	5	20	70
Natural Gas			
CO_2 removal	30	60	100
NGL removal and recovery	< 1	20	50
Other (N_2 removal, dehydration)	< 1	10	25
Vapor (C_{2+}) / Gas (N_2, Ar)	10	30	90
Vapor/Vapor (including dehydration)	5	20	100
Air dehydration/other	10	30	60
TOTAL	160	340	730
Annual growth %		8%	8%

EMERGING GAS AND VAPOR SEPARATION APPLICATIONS

The four emerging separation areas (hydrogen/vapor, NGL removal and recovery from natural gas, vapor/gas and vapor/vapor) have in common the presence of significant amounts of hydrocarbon vapors in the mixture to be separated. These vapors interact much more strongly with the membrane material than gases do and this has a bearing on the selection of the membrane materials. A brief description of the four emerging separation areas follows.

Hydrogen/Vapor Separations
Refineries are increasingly deficient in hydrogen supply because of an increase in hydrocracking and hydrodesulfurization operations. The increase is the result of tighter environmental regulations covering the products produced by the refinery. The most attractive option to increase the availability of hydrogen is to recover hydrogen from refinery off-gases, which currently are used as fuel. The typical hydrogen content of these off-gases varies from a low of 20% to a high of 90%. The four major hydrogen sources to be explored are:

(1) Refinery Fuel Gas, 20 to 40% hydrogen
(2) Pressure Swing Adsorption Tail Gas, 25 to 40% hydrogen
(3) Fluid Catalytic Cracker Off-Gas, 20% hydrogen
(4) Hydrocracker Purge Gas, 50 to 90% hydrogen

A high hydrogen content is desired for economical hydrogen recovery. However, off-gases with low hydrogen concentrations contain substantial amounts of C_{3+} hydrocarbons. In certain cases the simultaneous recovery of the C_{3+} fraction as liquified petroleum gas (LPG) can improve the overall economics of the hydrogen recovery operation.

NGL removal and recovery from natural gas
The propane and higher hydrocarbon fraction of natural gas is often referred to as natural gas liquids (NGL). The partial removal of the NGL fraction from natural gas is desired:
(1) to reduce the hydrocarbon dewpoint and/or the fuel value of the gas prior to entering the pipeline system,
(2) to condition the gas prior to its use as fuel for a compressor or turbine, and
(3) to utilize the NGL fraction as chemical feedstock rather than as a fuel.

The conventional technologies for NGL removal are condensation at low temperatures achieved by Joule-Thomson cooling or by refrigeration. The advantage of the membrane system is that the NGL fraction of the gas is enriched, which allows condensation at ambient temperatures.

Vapor/Gas Separations
Of the four emerging applications, the vapor/gas application is the most developed. Worldwide over 50 commercial installations are in operation for:
(1) the recovery of vinyl chloride during the manufacture of poly(vinyl chloride),
(2) the recovery of propylene during the manufacture of polypropylene,
(3) the recovery of ethylene during the manufacture of polyethylene,
(4) the recovery of ethylene during the manufacture of ethylene oxide and vinyl acetate, and
(5) the recovery of gasoline vapors from vent streams.

The common thread of the first four applications is that, in many processes, feedstock chemicals are lost in reactor purge and other vent streams. The capability of membranes to economically recover these chemicals has been demonstrated, and this application area is expected to show continued growth.

Vapor/vapor separations.
The separation of different hydrocarbons is typically performed by distillation, requires a large capital investment and represents the largest use of energy on the chemical processing industry. There is a huge potential for membranes to improve the efficiency of distillation and perhaps even to replace distillation in some cases. This application is very challenging, however, particularly with respect to the selection of membrane materials.

To date there is one commercial vapor/vapor membrane separation application: the vapor-phase dehydration of alcohols, primarily isopropanol. This separation is relatively easy as it is applied to a hydrocarbon/water mixture, rather than a mixture of two hydrocarbons. This is also the first application in which inorganic membranes are applied commercially. In addition to dehydration applications, the vapor/vapor application that attract the most interest at this time is olefin/paraffin separation (ethylene/ethane and propylene/propane).