

# Olefin/Paraffin Separation Technology: A Review

R. Bruce Eldridge

Phillips Petroleum Company, Bartlesville, Oklahoma 74004

A review of traditional and nontraditional technologies for the separation of light olefins and paraffins is presented. The technologies addressed range from conventional low-temperature distillation to chemical complexation using copper and silver ions.

## Introduction

A recent DOE study estimates that 0.12 Quads of energy (1 Quad =  $10^{15}$  BTU) is used yearly for olefin/paraffin distillation (Humphrey et al., 1991). The capital cost for a world-class ethylene unit currently exceeds \$500 million. A major part of this cost is the olefin/paraffin separations train. This large energy and capital investment requirement provides the incentive for ongoing olefin/paraffin separation technology research.

A significant amount of the light olefins produced during the refining of crude oil is used as refinery fuel. As natural gas supplies in North America decline, the need to conserve and recover these olefins will become critical. Cost-effective separation technologies will be required that can withstand the harsh operating environment of a petroleum refinery. In addition to traditional refinery and olefin plant applications, paraffin dehydrogenation units for the production of olefins from natural gas liquids (NGL) have recently been brought on stream. For these small units, typically less than 5000 bbl/day of olefin production, novel separation technologies may be competitive with more traditional unit operations.

Recent federal regulations, such as the Clean Air Act, mandate that hydrocarbon emissions from refineries and chemical plants be reduced to low levels. To reduce the economic penalty of environmental compliance, low-cost hydrocarbon separation technologies are required. For facilities located in nonattainment areas, the need to reduce hydrocarbon losses is especially critical. Facilities can no longer afford to dispose of waste hydrocarbon streams in their flare systems. Purge streams from polyolefin reactors and vents from polymer storage facilities, which were once flared, must be redirected to recovery systems. For streams containing a mixture of paraffinic and olefinic material, economic and process considerations may dictate that the olefin be recovered and recycled.

## Technologies

**Traditional Low-Temperature Distillation.** A typical separation scheme for the separation of ethylene and propylene from a light gas mixture is shown in Figure 1. For simplicity, gas treating and contaminant removal systems are not shown. The scheme is typical of the fractionation sequence used to recover olefins from ethylene reactor effluent streams and refinery catalytic cracker off-gases (Stobaugh, 1966; Tucker, 1959; Chrones, 1961). Low-temperature distillations are performed at elevated pressures in traditional trayed fractionators. The separation scheme is highly heat integrated with a cascaded ethylene/propylene refrigeration system typically used as the source of low-temperature cooling. This scheme has largely replaced the refrigerated lean oil absorption process for large-scale olefin recovery applications (Kniel, 1947). The use of a turbo-expander to produce the low temperatures required for the separation has also been investi-

gated (Minton, 1979). These systems are expensive to build and operate and are currently only economically attractive for streams containing high quantities of olefin, such as those from large refinery catalytic crackers and high-capacity ethylene crackers. The high level of heat integration requires that alternative separation technologies be carefully reviewed. Capital savings produced by replacing a fractionation step with an alternative technology can easily be offset by increased operating costs caused by losses in the unit's overall thermal efficiency.

**Extractive Distillation.** A typical process for olefin/paraffin separation by extractive distillation is shown in Figure 2. The solvent enters the column above the feed introduction point. Reflux of the overhead product reduces the amount of the solvent taken overhead. The solvent is typically a high-boiling polar compound.

A process for the separation of *n*-butane and 2-butenes is licensed by Krupp-Koppers (Emmrich, 1986). The process uses a solvent composed of a mixture of morpholine derivatives, which modifies the components' relative volatilities and makes fractionation feasible. The process yields a 2-butene recovery of 99% at a purity of 99 wt % from a feed containing 48 wt % *n*-butane and 52 wt % 2-butene.

The application of extractive distillation to the separation of propylene and propane is discussed by Kumar et al. (1972). On the basis of results from computer simulations, the study concludes that extractive distillation offers no advantage over traditional distillation for the hypothetical solvents studied. Detailed cost calculations were performed for an optimized extractive distillation processing scheme. The thermodynamic characteristics of the solvent have a major impact on the process economics, and the conclusions drawn in the paper are a direct function of the solvent properties used in the simulations. It is conceivable that solvents could be found which can be economically utilized for the olefin/paraffin separation.

**Physical Adsorption.** The use of molecular sieves to perform olefin/paraffin separations has been investigated by numerous researchers. 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) (Shu et al., 1990). Experimental and modeling results indicate that the approach is feasible for binary mixtures containing less than 25 mol % propylene. Additional data for the VTSD process is presented by Kulvaranon et al. (1990). Experimental results are given for the gas-phase separation of propane/propylene using 5A and 13X molecular sieves. The adsorption cycle was run at 25 °C and 1 atm. Desorption temperatures were stepped from 50 to 160 °C with propane preferentially desorbed at the lower temperatures. For a 50–50 mol % mixture, a cycle that includes recycle of the material desorbed at intermediate temperatures will

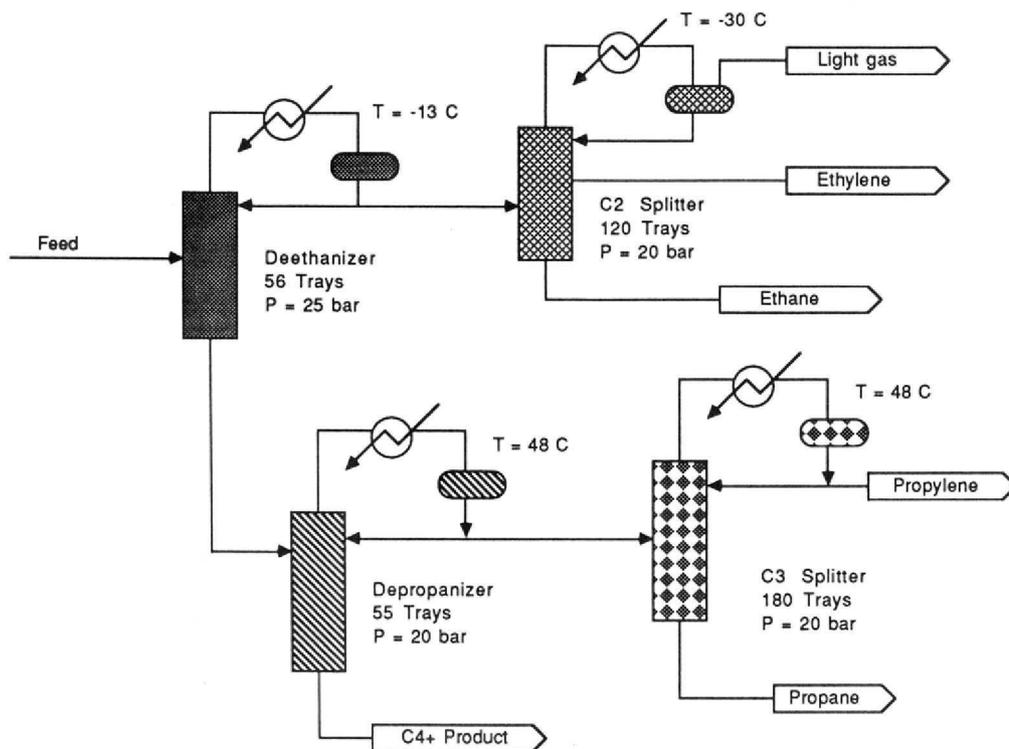


Figure 1. Conventional low-temperature distillation process for olefin/paraffin separation.

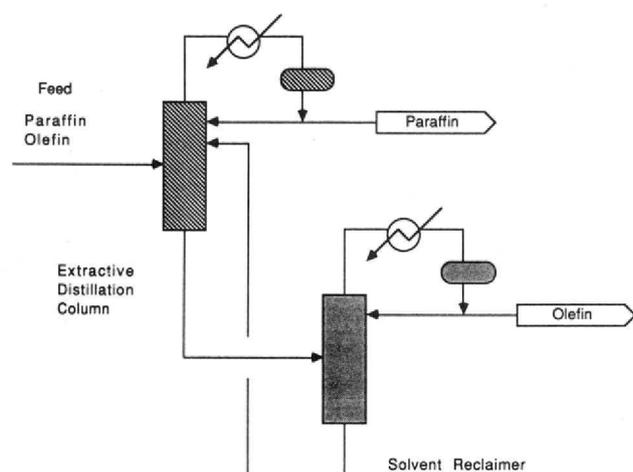
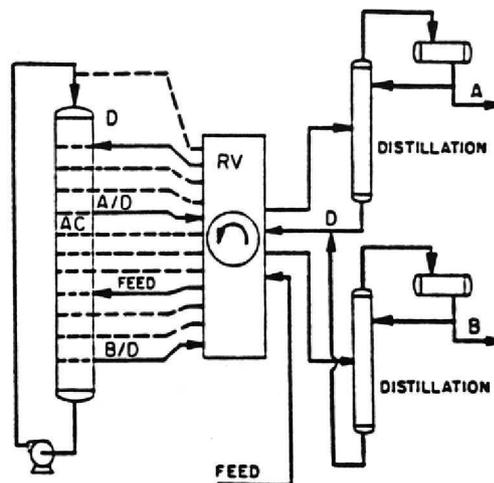


Figure 2. Typical extractive distillation process scheme.

produce an 85 mol % propylene product. Hydrocarbon loadings were 3.2 g of ethylene and 1.1 g of ethane per 100 g of adsorbent. An economic comparison indicated that the VTSD energy costs were lower, but capital costs were higher, than a comparable distillation process. A process configuration based on a hybrid adsorption/distillation system was considered to be an attractive commercial arrangement.

Experiments conducted with ion-exchanged molecular sieves indicate that significant separation can be obtained for olefin/paraffin mixtures (Schoellner and Mueller, 1986). K, Ba, and Mg ion exchanged zeolites were used in the tests. Favorable olefin separation yields were obtained for ethylene/ethane and propylene/propane binaries and mixtures of methane, ethane, ethylene, and propylene. Enhancement of the olefin yield was obtained as the exchanged ions were varied. Loadings per 100 g of adsorbent were 3.8 g of ethylene for K, 4.8 g for Ba, and 5.4 for Mg.

A commercial process for olefin/paraffin separation is licensed by UOP Inc. The "Olex" process uses a propri-



AC - ADSORBENT CHAMBER  
RV - ROTARY VALVE  
D - DISPLACEMENT AGENT  
A - ADSORBATE  
B - LESS-ADSORBED COMPONENT

Figure 3. UOP simulated moving bed process for olefin-paraffin separation.

etary adsorbent and desorbent fluid in combination with UOP's simulated moving bed adsorption technology (Figure 3). Reported pilot plant results indicate that high recoveries (99.7 wt %) and purities (99.6 wt % on a desorbent-free basis) can be obtained (Tajbl, et al., 1980).

**Chemical Adsorption.** The basis for chemisorption of an olefin by a metal complex is presented in Figure 4. The olefin  $\pi$  bonds interact with the  $\sigma$  and  $\pi$  bonds of the metal. Copper and silver ions are commonly used as complexing metals.

Ethylene adsorption results are reported using copper(I) chloride immobilized on a polystyrene resin having primary and secondary amino groups (Hirai et al., 1986a). The adsorption cycles were carried out at 20 °C and 760

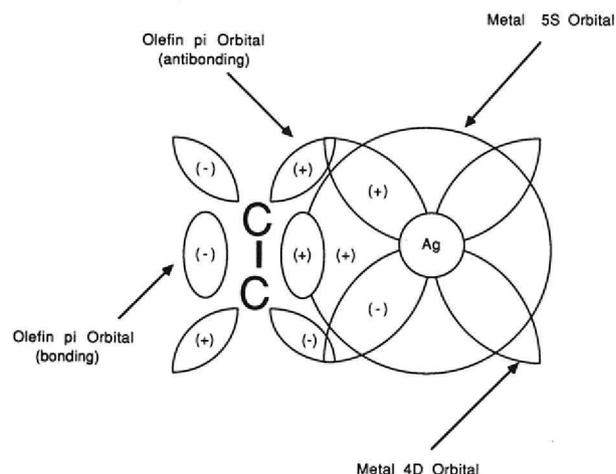


Figure 4. Metal-olefin coordination.

mmHg. The ethylene loading was 2.2 g/100 g of adsorbent. Combined pressure and temperature swing regeneration was used to remove the complexed olefin (80 °C and 5 mmHg). The adsorbent exhibited a selectivity of 5.9 for ethylene over ethane with no appreciable methane adsorption. Test results indicated that interaction of the copper(I) chloride with the polymer amino groups was necessary for ethylene adsorption.

Loadings of 5.6 g of ethylene per 100 g of adsorbent were obtained for an silver tetrachloroaluminate ( $\text{Ag}^+\text{-AlCl}_4^-$ ) adsorbent at 1 atm and 20 °C. An ethylene feed containing 0.6 mol % water was used in the tests (Hirai et al., 1985). The reactive aluminum silver chloride ions were protected from water attack by impregnation into the pore structure of a cross-linked styrene-divinylbenzene copolymer. Repeatable loadings were obtained after multiple process/regeneration cycles (regeneration at 8 mmHg at 20 °C).

Tests were conducted for the adsorption of carbon monoxide on an aluminum copper(I) halide adsorbent (Hirai et al., 1986b). The reactive complex was believed to be the double salt  $\text{Cu(I)AlCl}_4$ . The results have application to the adsorption of olefinic compounds. The equilibrium CO loadings were 3.8 g of CO per 100 g of adsorbent following a 7 mmHg 20 °C regeneration. Loadings decreased significantly with increasing temperature. Experiments which substituted aluminum bromide, copper(I) bromide, aluminum iodide, and copper(I) iodide for copper(I) chloride did not produce loadings greater than the base complex. Carbon disulfide and dichloromethane were the best solvents for the adsorbent preparation.

The patent literature contains several examples of metal-based adsorption. A process which uses a copper(I)-based adsorbent on carbon is outlined (Hirai et al., 1988). The examples given in the patent indicate that ethylene can be adsorbed from a mixture of nitrogen (10 mol %) and ethylene (90 mol %) at 760 mmHg and 20 °C. Essentially complete desorption is accomplished at 760 mmHg and 100 °C. The presence of the metal increases the olefin loading substantially over the loading exhibited by unmodified carbon. A similar approach, using ion-exchanged faujasite is also reported (Pearce, 1988). Sodium Y zeolites are contacted with a cupric nitrate solution with approximately 60% of the  $\text{Na}^+$  cation being exchanged to form a Cu-Y adsorbent. The active form of the adsorbent, Cu(I), is formed by heating the adsorbent in the presence of carbon monoxide. Selectivities at 1 bar and 20 °C of 217/1 are reported for the adsorption of ethylene from methane

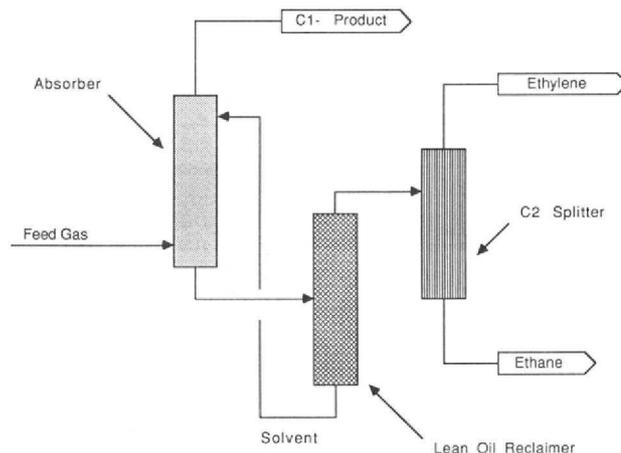


Figure 5. Lean oil absorption process for the recovery of olefins from polyethylene plant vent streams.

Table I. Typical Feed and Product Streams for a Lean Oil Recovery Unit

component	feed (mol %)	product (mol %)
hydrogen	2.5	0.0
nitrogen	37.5	0.0
methane	0.5	0.5
ethylene	57.5	99.0
ethane	1.0	0.5
heavier olefins	0.5	0.0
heavier hydrocarbons	0.5	0.0

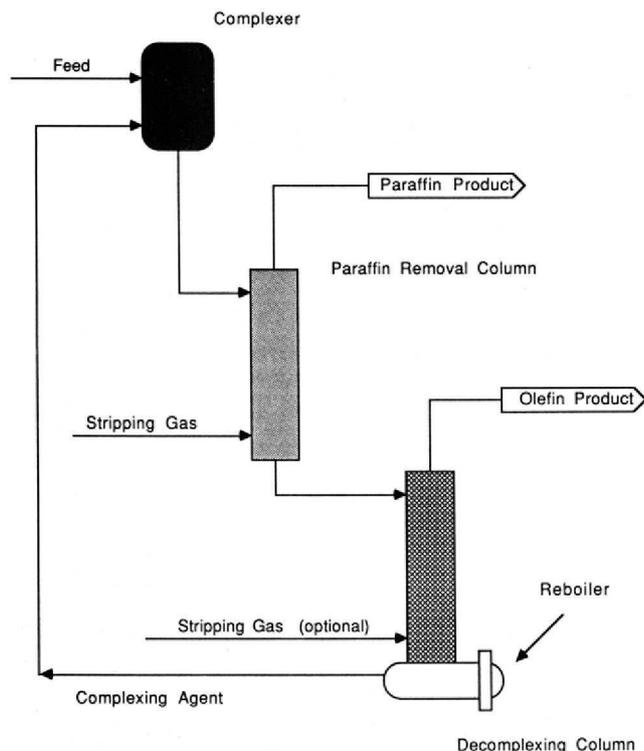
and 2.8/1 for the adsorption of ethylene from ethane. Regeneration is accomplished by pressure swing.

**Absorption. 1. Physical Absorption.** A lean oil absorption process for the recovery of light hydrocarbons is shown in Figure 5. This process has been reported to offer cost advantages over traditional cryogenic recovery technologies for the recovery of olefins from polyethylene plant vent streams, (Fatemizadeh and Nolley, 1990). The lean oil is typically a  $\text{C}_{5+}$  range material. As mentioned in a previous section, lean oil absorption technology is not new. However, it had not been widely applied to the recovery of olefin streams from waste vents. Table I indicates that the lean oil process will produce olefin of sufficient purity to be recycled to a polyolefin reactor.

**2. Chemical Absorption.** Silver- or copper-based absorption processes offer potential for olefin recovery. The absorption process takes advantage of the molecular interaction detailed in Figure 4. A diagram of a complexation process is given in Figure 6. The feed contacts the complexing solution in a sparged vessel, and the complexed olefin and noncomplexed paraffin exit the vessel and flow to a paraffin recovery column. The bottoms product from the paraffin tower is passed to a second column where the olefin is liberated from the complex by elevated temperature or gas stripping.

A detailed review of olefin complexation by cuprous salts is given by Blytas (1992), and a complete review of olefin recovery by aqueous silver nitrate solutions is given by Keller et al. (1992). Both references present fundamental theory and practical considerations. A detailed discussion of the use of solid copper salts for the separation of olefins is given by Long (1972). Various salt preparation procedures are given and process considerations are addressed.

A commercial process which utilizes a bimetallic salt is detailed by Gutierrez (1978). The process, licensed by Tenneco, is based on a cuprous aluminum tetrachloride salt dissolved in an aromatic solvent, such as toluene. The process ethylene recovery is approximately 96% at 99.5%



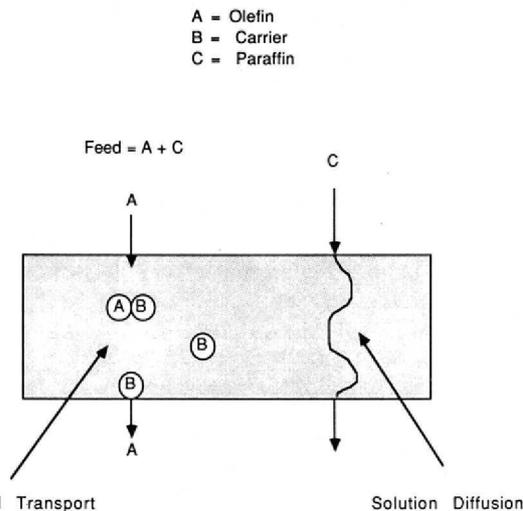
**Figure 6.** Liquid-phase absorption process based on metal complexation.

purity from a refinery gas containing 12% ethylene. A combination of pressure reduction and thermal swing is used to regenerate the complexing agent. Significant feed pretreatment is required to remove feed contaminants, such as  $H_2S$  and  $CO_2$ , which will interfere with the complex formation or destroy the complexing agent.

The use of cuprous diketonate for olefin recovery has been explored by Ho (1988). Separation factors of 17/1 were obtained for ethylene/ethane and 10/1 for propylene/propane using cuprous diketonate in an  $\alpha$ -methylstyrene solvent. The experimental results indicate that the solvent participates in the complexation process by forming a weak bond with the complexing agent. This weak bond stabilizes the complexing agent in the absence of a reactive olefin adsorbate. The agent is also capable of separating branched and unbranched olefins based on steric effects. Separation factors of 2.0 are reported for the separation of 1-pentene and 2-methyl-2-butene.

**Membrane Separation.** The use of metal-based facilitated transport membranes has been studied for a variety of olefin/paraffin separations. The transport mechanism is shown in Figure 7. The olefin (A) forms a reversible complex with the metal carrier (B). The complex migrates across the swollen membrane film releasing the olefin on the opposite side of the membrane. The flux rate of olefin is determined by the diffusion rate of the complex through the film. The amount of olefin transported is a function of the flux and the concentration of metal carrier in the membrane.

Steady-state fluxes for the separation of styrene and ethylbenzene were reported for sodium- and silver-exchanged perfluorosulfonate ionomer membranes (Koval et al., 1989). Separation factors (styrene/ethylbenzene) ranged from 8 to 36 for the  $Ag^+$ -exchanged material. Nafion 117 and an experimental Nafion material (NE 111) were used in the study. The polymer was converted from the  $H^+$  form to the  $Na^+$  and  $Ag^+$  forms by contact with sodium hydroxide and silver nitrate. Flux measurements were made using a two-compartment stirred cell. The com-



**Figure 7.** Facilitated transport mechanism.

partments contained isooctane and the membrane swelling agent, water, or a 50/50 water-ethanol mixture. Measurements showed that the  $Na^+$  membrane exhibited low hydrocarbon fluxes for both ethylbenzene and styrene. In contrast, the styrene-facilitated flux for the  $Ag^+$  form is approximately 2 orders of magnitude higher than that for the  $Na^+$  form. Higher separation factors were obtained for water-swollen membranes while higher fluxes were obtained for the water-ethanol-swollen membranes. Fluxes for the NE 111 material were higher for both swelling agents at similar styrene/ethylbenzene selectivities. This result was attributed to thickness, solvent content, and structural differences. It was suggested that the facilitated transport mechanism occurred by either mobile diffusion of the  $Ag^+$ -solute complex through the swollen membrane or by movement of the olefin across fixed silver sites, a "hopping" mechanism.

A silver-containing sulfonated polyphenylene oxide membrane has been developed (Leblanc et al., 1980). The silver ion was impregnated into the polymer matrix by ion exchange. The authors contend that the ion exchange mechanism anchors the facilitating agent into the membrane film more effectively than a surface tension based mechanism. The ethylene/ethane selectivity through the membrane was 288/1.

A detailed study of olefin/paraffin separation on silver-impregnated cellulose acetate membranes was conducted by Hughes et al. (1986). Results were reported for flat sheet and hollow fiber configurations. Hollow fiber systems were tested in both laboratory and field locations. Flat sheet permeation tests were conducted in a modified Millipore cell. The feed gas was water-saturated ethylene. Water-saturated helium was used as the permeate purge fluid. Laboratory-scale hollow fiber modules were constructed by potting cellulose acetate fibers in 1/4- and 1/2-in.-diameter stainless steel tubing followed by impregnation with silver nitrate. Field tests were conducted with silver-impregnated commercial hollow fiber permeators (membrane area = 240–400 ft<sup>2</sup>). The test feed gas to the unit, from a commercial polypropylene unit, was 75 mol % propylene, with the balance being methane, ethane, and propane. Liquid-phase hexane was used as the permeate purge stream. The feed was supplied to the bore side of the permeator at 190 psia. Studies conducted for a 60-day period indicated that the permeation rate decreased by a factor of 5 during the test, with a steady decrease the first 15 days of the test. The initial flux was 0.175 cm<sup>3</sup>(STP)/(cm<sup>2</sup> min). The olefin selectivity re-

mained above 92% for the entire test. The loss in performance was attributed to loss of water and  $\text{Ag}^+$  from the membrane film. A fundamental model was developed which accurately fit the initial hollow fiber data, but did not account for the decrease in membrane productivity.

### Summary and Conclusions

This review indicates a significant amount of research has been conducted on olefin/paraffin separation technology. However, there are currently only a very few nondistillation processes being used in the chemical and refining industry. This is due in part to the conservative nature of the refining and petrochemical industry. There are inherent properties of the new technologies which have negatively impacted their acceptance. The unpredictable nature of the separations unit feedstock impacts the use of new olefin/paraffin technologies. Technologies, such as metal-based absorption, which are susceptible to deactivation by feed contaminants may not be acceptable for applications where tight control of the feed composition is not possible. The addition of feed pretreatment steps negatively impacts the process economics and may make the new technology impractical. Facilitated transport membranes have similar contamination problems, along with the need for water content control. The addition of water into the separating device's feed can also cause problems in downstream processes. For polyolefin plant applications, water must be removed from the olefin stream prior to introduction into the polymerization reactor. This dehydration step adds additional cost to the separation system. Chemical adsorption systems suffer from low olefin loadings (<5 wt %) and contamination problems. Physical adsorption olefin loadings are low, and the process and regeneration cycles are complicated.

With all these complications and problems, it appears more research is needed in order to find an acceptable replacement for distillation. The potential for energy and capital savings is significant, provided the technical and economic hurdles can be overcome. A good start has been made, and further research will provide the technologies needed to meet environmental and raw material needs for the next century.

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Received for review December 29, 1992

Accepted March 22, 1993\*

\* Abstract published in *Advance ACS Abstracts*, August 15, 1993.