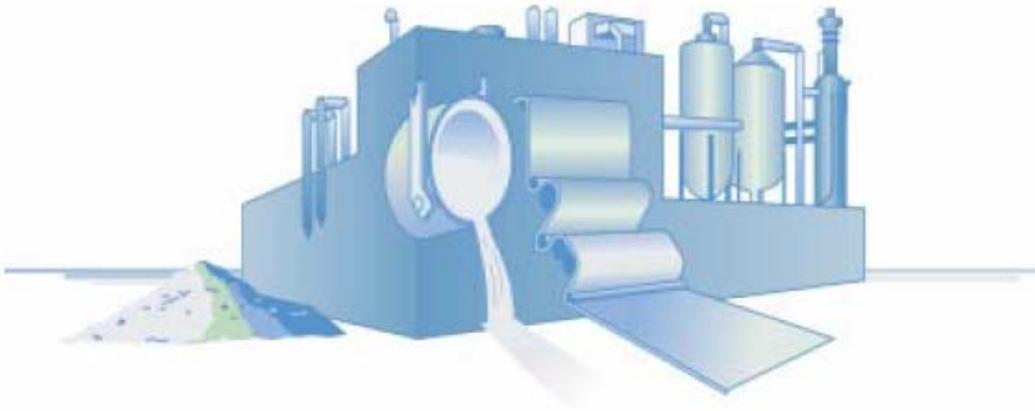




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Industrial Technologies Program

Hybrid Separations/Distillation Technology: Research Opportunities for Energy and Emissions Reduction



April 2005

Study conducted for the U.S. Department of Energy by the University of Texas at Austin, the Oak Ridge National Laboratory, and the American Institute of Chemical Engineers.

Preface

The U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (DOE/EERE), Industrial Technologies Program (ITP) supports research and development (R&D) to improve the energy efficiency and environmental performance of industrial processes. The program's primary role is to invest in high-risk, high-value R&D projects that will reduce industrial energy requirements while stimulating economic productivity and growth.

ITP's Chemicals subprogram supports R&D relevant to the chemical industry. This report, *Hybrid Separations/Distillation Technology: Research Opportunities for Energy and Emissions Reduction*, focuses on improving the existing separations systems for the two largest energy-consuming sectors: the chemicals and petroleum refining industries. It identifies the technical challenges and research needs for improving the efficiency of distillation systems. Areas of growth are also highlighted.

Information for this report was gathered from a variety of sources, including ITP planning documents, industrial visions and roadmaps, and a two-day workshop hosted by the Separations Research Program at the University of Texas at Austin. It was initiated and funded by the ITP Chemicals subprogram and overseen by and R. Bruce Eldridge and A. Frank Seibert of the Separations Research Program at the University of Texas at Austin, Sharon Robinson of the Oak Ridge National Laboratory, and Jo Rogers of the American Institute of Chemical Engineers.

This report was funded by the ITP Chemicals subprogram and is intended to be used to focus technology development for reducing energy use and environmental emissions in the chemicals and petroleum refining industries. It will be a useful strategic planning tool at DOE for assessing future directions in R&D conducted under the ITP Chemicals and Petroleum Refining subprograms.

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Foreword

The purpose of this report is to identify opportunities for research in both hybrid and distillation technologies that will lead to large reductions in energy use and environmental emissions. This report focuses on improvement opportunities for existing industrial separations applications and touches on growth areas, such as energy-intensive distillation separations; n-paraffin and iso-paraffin separations; synthesis gas separation; and hydrogen, carbon monoxide, and carbon dioxide separations critical for the “hydrogen economy.” The most energy-intensive flow sheets in the chemical and petroleum industries were reviewed for opportunities to implement these improved separation technologies.

It is recognized that reduction of energy used for separations can also be accomplished with enhanced upstream reaction units that will lower the demands on subsequent separation steps, or by replacing existing process flow sheets with totally new concepts that would reduce or eliminate the need for high energy separations. Neither approach was addressed in this report.

While this report presents a compilation of research needs and opportunities, the data-gathering activities were limited by time, scope, degree of participation, and the boundaries imposed on the subject area. As a result, the report may not fully capture all viewpoints. Although efforts were made to incorporate a broad range of views, some valid ideas may have been excluded based on judgments made in combining and prioritizing information to produce a final report.

Executive Summary

Energy used to drive separation processes accounts for approximately sixty percent of the total energy used by the chemical and petroleum industries. The amount of energy consumed by distillation processes is much larger than the energy used to drive all other separation processes combined. The substitution of a more complex, higher-investment but lower-energy-usage process for an existing distillation process has truly an uphill fight to be economically viable, due to the large sunk capital investment in existing plants, the slow rate of plant replacements, and the diverse numbers of applications where distillation is utilized.

This report evaluates opportunities to meet the challenge of developing economically-attractive process technologies that will lead to substantial reductions in energy use (greater than one trillion Btu/yr) and emissions. Focusing on the existing practices of the two largest energy consuming industries (chemicals and petroleum refining), this report identifies areas for the Department of Energy (DOE) Energy Efficiency and Renewable Energy (EERE) Industrial Technologies Program (ITP) where large energy savings could be realized by developing and implementing improved distillation systems. Since most new builds are in growth areas outside of the U.S.A., technologies that would enable plant debottlenecks for U.S. applications are the focus of this report. Debottlenecking opportunities (improvements that increase the throughput of existing distillation systems) include making improvements to existing distillation columns and development of hybrid systems.

Reducing energy usage in distillation, especially in separations with low relative volatilities, or ones that operate at cryogenic or very high temperatures, represents a major research opportunity for ITP. The most fruitful areas to study for energy-use reduction to augment distillation with lower-energy-use processes are solvent extraction and, secondarily, adsorption. Several technical challenges were identified for these technologies, and there are numerous high-energy applications for the processes if implementation barriers can be overcome. Process intensification and equipment with reduced solvent and sorbent inventory will make possible the use of higher priced, but more selective, mass-separating agents. Applications for membrane hybrid systems are likely to be limited to “clean” applications, and significant investment in membrane technology has already occurred with limited industrial implementation. Focused research is recommended in this technical area. Few opportunities were identified for crystallization and absorption hybrid systems.

Opportunities for improving equipment in existing distillation systems included divided wall columns, improved packing designs, heat integrated distillation, and improving mass transfer efficiencies. A better fundamental understanding of mass transfer, gas/liquid contact area, and multicomponent data are needed to improve packing designs and mass transfer efficiencies. Independent technical reviews of industrial experiences to date and pilot-plant demonstrations are needed for wide-spread implementation of divided wall columns and heat integrated distillation systems.

The debottlenecking opportunities described above can not be implemented generically across the industry; they will be process flow sheet specific. Hybrid systems and improved equipment systems are already being used to a limited extent within the industry, and there are improved mass separating agents and process equipment on the market today that are not being used extensively by the industry for debottlenecking plants. This is in part due to lack of tools to evaluate their performance for specific applications.

To overcome the market acceptance and economic barriers, enabling tools that will allow evaluations at the plant-specific level are critical in the development of improved distillation technologies. Development of complete process simulation packages for all candidate separations technologies and the acquisition of the experimental data required to permit accurate performance predictions are priority R&D needs. These R&D needs are cross-cutting and are pre-competitive. They are prime candidates for an ITP R&D program.

R&D directed at the development of new and enhanced mass-separating agents and process equipment without a specific process focus is useful for creating new knowledge. However, the results will not necessarily transfer to successful incorporation into industrial applications. Successful capture of these opportunities will most likely occur when R&D efforts are focused on specific applications. Unfortunately, process specific R&D often involves intellectual property issues and could fall into the realm of competitive research, not typically funded by ITP. Areas for application-specific research studies will need to be evaluated carefully before being pursued.

1. Introduction

The chemical industry is the largest consumer of energy of the manufacturing industries. It represents 6% of all domestic energy use and 24% of the total U.S. manufacturing energy use. Petroleum refining is the second largest consumer of energy, accounting for approximately 10% of the total U.S. manufacturing energy use. Separations account for approximately 60% of the in-plant energy usage for these two industries. Distillation operations account for ~95% of the total separation energy used in the refining and chemical processing industries with ~40,000 distillation columns operating in over 200 different processes. This high usage rate is primarily due to distillation's flexibility, low capital investment relative to other separations technologies, and low operational risk. Unfortunately, the energy efficiency of a commercial distillation column is low with a thermodynamic efficiency of less than 10 percent being typical.

On the surface, distillation would appear to be a favorable R&D target area with huge potential energy savings. In reality, it will be a formidable challenge to develop improvements or replacements for distillation to achieve significant energy savings, due to the large sunk capital investment in existing plants, the slow rate of plant replacements, and the diverse numbers of applications where distillation is utilized. Multiple R&D pathways (and often application-specific R&D) will be required for overcoming the barriers to implementing replacement separation technology.

There are four options for saving energy in distillation:

- Make the process itself more energy-efficient.
- Augment it with advanced processes to form energy-efficient hybrid systems.
- Replace it with an alternative separations technology.
- Improve reaction steps in existing flowsheets or develop new process flow sheets to reduce or eliminate the need for distillation.

A balanced R&D portfolio will be required, with research in each of these areas, to achieve DOE's objective of reducing a significant amount of the distillation energy usage.

This report identifies research needs which will lead to the implementation of hybrid processes. Successful implementation of these hybrid processes will significantly reduce the energy consumption of separations schemes by supplementing the capability of distillation columns with another separations technology. This approach also takes advantage of existing depreciated capital investment while adding novel emerging separations technology to produce an optimum separation scheme.

The report also identifies research needs which will lead to breakthrough technology innovations in distillation equipment design. While most advances in distillation equipment design have been incremental to date, the potential exists for step changes in mass transfer and heat transfer equipment. Even small improvements in distillation column operation can produce major energy savings.

Background information used for this report include three studies which have extensively reviewed the chemical and petroleum manufacturing processes for total energy use, energy use by separation processes, and potential energy savings from R&D in separations technologies: *Materials for Separation Technologies: Energy and Emission Reduction Opportunities* (DOE ITP draft report, December 13, 2004), *Chemical Bandwidth Study* (DOE ITP, December 2004), and *Separation Process Technology* (J. L. Humphrey and G. E. Keller II, McGraw Hill, 1997) . Major results are summarized in Tables 1.1 and 1.2.

Table 1.1 Domestic Distillation Energy Usages

Feed	Typical Components Light/Heavy	Estimated Energy Use, quads/yr
Petroleum	Gasoline/naptha	0.49
Crude oil	Light naptha/heavy naptha/light distillate	0.42
Liquefied petroleum gas (LPG)	Ethane/propane/butane	0.22
Olefins	Ethylene/ethane, propylene/propane	0.12
Miscellaneous hydrocarbons	Cumene/phenol, acetone/acrylonitrile	0.10
Water-oxygenated hydrocarbons	Methanol/water, water/acetic acid	0.10
Aromatics	Ethylbenzene/styrene, benzene/toluene	0.08
Water—inorganics	Ammonia/water	0.06
Air	Nitrogen/oxygen	0.02
Other		0.31
Total reboiler energy		1.9
Total fuel requirement ¹		2.4

¹ Fuel requirement was estimated based on an average boiler efficiency of 80%.

Source: *Humphrey and Keller, Separation Process Technology, McGraw-Hill, 1997, page 292*

This report refined the list of industrial process flow sheets that are likely to benefit from improved separation technologies (See Table 2.1) and identified R&D needs which are likely to have a high probability of meeting the above implementation criteria from an industrial perspective. Technologies considered for future R&D projects should be applicable to these industrial processes and should be evaluated for technical feasibility, economic feasibility, and energy savings potential. Criteria required for industrial implication of distillation R&D include:

- Technologies proposed to augment existing distillation columns to increase output should have a payback of 12 – 18 months.
- Technologies proposed with energy reduction improvements should have a payback of 6 – 12 months.
- Each technology proposed to reduce energy usage should provide savings exceeding one trillion BTU/yr at full implementation across the industry

Table 1.2 High-Energy Distillations Appropriate for Technology Improvement R&D

- Olefin-paraffin separations:
 - ethylene/ethane
 - propylene/propane
 - styrene/ethylbenzene
 - Isomer separations:
 - *p*-xylene/mixed xylenes
 - *n*-paraffins from isoparaffins
 - Removal of organics from water where azeotropes are formed:
 - ethanol
 - isopropanol
 - Recovery of dilute organics from water:
 - acetic acid
 - ethylene glycol
 - Miscellaneous hydrocarbons:
 - cumene/phenol
 - Inorganic chemicals:
 - ammonia
 - phosphoric acid
-

Adapted from *Humphrey and Keller, Separation Process Technology, McGraw-Hill, 1997, page 292*

2. Hybrid Systems

To date hybrid systems have seen limited use in the chemical and petroleum industries. Reverse osmosis is used to concentrate wastewater feeds to evaporators as well as organic acid/water feeds to distillation columns. Pressure swing adsorption units, using molecular sieves, are used to dehydrate azeotropic mixtures. Pervaporation membranes are used for both purposes. Industrial experience has been that marginal payouts are to be expected if energy savings is the only benefit. (Humphrey and Keller, 1997). In addition, there are improved mass separating agents on the market today that are not being used extensively by the industry.

This report identified high-priority application areas, technical opportunities, and enabling technologies required to overcome the barriers to implementation of distillation hybrid systems. Hybrid processes were evaluated to identify R&D required to significantly reduce the energy consumption of separations schemes by supplementing the capability of distillation with another separations technology. This includes augmentation and/or retrofitting of existing distillation columns with alternative technologies (membranes, adsorption, extraction, crystallization, absorption, etc.) to debottleneck processes and reduce energy use. It does not assume that changes in other parts of chemical flow sheets (new catalysts, new reactors, etc.) will be made to reduce the load on separations equipment. This approach takes advantage of existing depreciated capital investment, while adding novel emerging separations technology, to produce an optimum separation scheme. High-energy distillations considered appropriate for improvement by hybrid systems are shown in Table 2.1.

Several R&D opportunities for hybrid systems were identified for the chemical industry, primarily for adsorption, extraction, and membrane separations. Fewer opportunities with significant energy-saving potential were identified for absorption and crystallization. Although distillation is the major consumer of energy in the refining industry, few practical opportunities were identified. Membranes and adsorbents could potentially augment distillation for relatively “clean” refining separations, such as gas recovery. Recommendations are discussed below and summarized in Appendices 3 and 4.

Implementation of hybrid systems to achieve debottlenecking will be technically easier and more economical than replacing distillation systems with alternative technologies. For example, most membrane processes today cannot produce the high-purity products required of distillation applications. However, it may be possible to make technical advances that will take advantage of their overall energy efficiency by using membranes as a pretreatment step followed by a traditional distillation step. Recent advances in the development of new solvents also make extractive distillation a potentially viable alternative. Distillation-adsorption hybrid processes involving a rough separation with distillation followed by polishing with adsorption also have promise.

Chemical production and petroleum refining are mature, highly capital-intensive, and competitive industries. These factors, and the long economic life of existing facilities, are

Table 2.1 Distillation Systems Appropriate for Hybrid Technology Implementation

Hybrid Distillation System	Application	Petroleum Refining	Caustic Soda/Chlorine	Olefin/Paraffin	Phosphoric Acid Recovery	Ammonia/CO2 Recovery	Oxygen/Nitrogen	Cumene/Phenol	Organics from Water	Acids from Water	p-Xylene Recovery	n-iso Paraffin Separation	Hydrogen	Ethyl benzene	Xylenes	Methanol	Natural Gas Dehydration	Syn Gas/Hydrogen
Adsorption	Integrated Liquid Phase Adsorption	X	X	X	X			X	X	X				X	X	X		
	Bulk Adsorption	X	X	X	X	X	X	X					X	X	X	X		
Extraction	Debottlenecking			X	X			X		X	X	X						
	Azetrope breaker								X									
Membrane	Azetrope breaker			X					X									
	Prefractionate Liquid			X			X										X	
	Bulk Gas Cuts																X	
	Syn Gas Ratio Improvements																	X
	Vent (Off-Gas) Recovery	X		X														
Crystallization	Desalination/Reverse Osmosis		X		X													
	Crystallization							X			X							
	Melt Crystallization										X	X						
Absorption	Freeze Concentration		X		X													
						X							X					

deterrents to the implementation of economic, large-scale, non-conventional, energy-saving separation technologies. The economic realities of replacing existing equipment must be incorporated in technology development planning.

To overcome the market acceptance and economic barriers described above, new and advanced separation materials must be developed with superior performance (higher selectivity, higher flux, etc.). In addition, the separating materials and the equipment housings in which the process operates must be more tolerant of harsh environments. However, improvements in the separating agents as well as in the materials of construction for the processing equipment are likely to increase the costs of the alternative processes, making economics unfavorable. Therefore, new equipment design will be required to make new technology implementation economically feasible. Enabling tools that will allow evaluations at the plant-specific level are also critical in the development of improved distillation technologies. Without these tools, new advances in mass separating agents and improved equipment designs will not be widely implemented by industry.

Adsorption Hybrid Systems

Hybrid distillation-adsorption processes involve making a rough separation with distillation followed by polishing with adsorption. There are many opportunities for R&D that could be implemented in high-energy process flow sheets as shown in Table 2.1 Reference documents suggest that high-priority hybrid distillation-adsorption processes should include hydrocarbon-water, oxygenated hydrocarbons-water, olefins, and aromatic separations (J.L. Humphrey and Associates, *Separation Technologies – Advances and Priorities*, DE91-010-024, February 1991). Therefore, the potential energy savings for such systems are high.

However, the development of new effective adsorbents with increased bed loading, and reduced energy required per regeneration will be needed. Development of improved adsorbents requires understanding the connection between properties of adsorbents and their performance. New adsorbents must be developed that will selectively adsorb components from close-boiling hydrocarbon mixtures.

Application Areas

- Integrated Liquid Phase Adsorption
- Bulk Adsorption

Technical Opportunities

- Public adsorbent performance data base
- Molecular simulation of solute – adsorbent interaction
- Molecular design of adsorbents
- Development of fouling resistant adsorbents or guard bed technology
- Optimization and integration of PSA cycles

Barriers

- Recognition of strategic importance
- Lack of understanding of surface chemistry/physics at molecular level
- Computational power
- Lack of adsorbent data, design methodology and novel materials
- Lack of pooled experimental data
- Narrow range of experimental data

Enabling Technologies

- Integrated process simulator to model complete hybrid process
- Molecular simulation
- Advanced computational capability

Extraction and Absorption Hybrid Systems

Hybrid extraction-distillation processes generally involve transferring a component of a liquid mixture into a solvent followed by an easy distillation to separate the solvent and transferring component. There are many opportunities for R&D which could be implemented in high-energy process flow sheets as shown in Table 2.1. One variation is

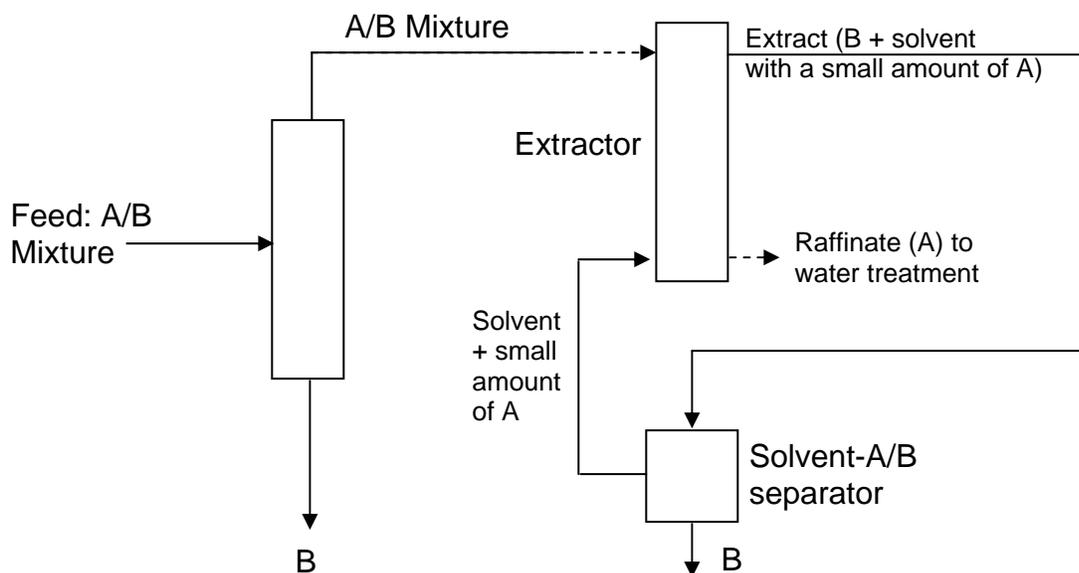


Figure 2.1 Example Extraction/Distillation Hybrid System for Acetic Acid (B) / Water (A) Separation with Ethyl Acetate as the Solvent.

shown in Figure 2.1. In this example that involves the separation of acetic acid and water, the extraction column is used to relax the separations requirements of the distillation tower and reduce the overall energy consumption. Absorption, which involves the transfer of a component of a gas phase to a liquid phase in which the gaseous component is soluble, has R&D needs similar to those for extraction but there fewer high-energy process applications (See Table 2.1).

For hybrid processes involving solvent extraction and absorption to be economically competitive with distillation, efficient solvents will be needed. Next generation solvents must have greater resistance to chemical and thermal degradation and improved solubility and emulsification characteristics. These solvents must be able to be “tuned” for high selectivity for specific separation applications and must also provide for rapid mass transfer and phase separation. In addition to solvent development requirements, the lack of an adequate solvent screening procedure results in costly experimental evaluations. A rapid solvent screening tool would significantly reduce the cost of developing new solvents.

Solvent extraction and absorption have traditionally been characterized by relatively large equipment sizes per unit throughput. In some cases, the potential energy savings from technological innovations may allow economic use of new relatively expensive solvents, such as ionic liquids, in these systems. Depending on the thermodynamic driving force, processes may require such large solvent inventories that they would not be economically competitive with distillation. In these cases, new equipment designs that minimize solvent requirements may be critical to implementation.

Process intensification should be achieved by identifying efficient solvents and equipment plus creative implementation of extraction within the overall process flow sheet. Efficient equipment designs that can be scaled up to handle large-scale production rates in order to take advantage of economics of scale should be developed. Benefits can be obtained from the refinement of existing equipment designs (such as more efficient column internals) and improved design methods.

Industry is often reluctant to adopt new separation technologies such as liquid-liquid extraction or extractive distillation because of the lack of familiarity with the fundamental concepts. New process conceptualization tools are needed to improve the utilization of liquid-liquid extraction and extractive distillation. Such tools could be implemented in a commercial process simulator.

There is a lack of available phase equilibrium data especially at low solute concentrations where the activity coefficients can change significantly. Existing models, such as UNIFAC, are not applicable to complex multifunctional solvents. New phase equilibrium estimation methods need to be developed. There is also a lack of available mass transfer and hydraulic data that would be useful during scale-up. In addition, rapid small-scale tests for solvent mass transfer are needed for screening extraction equipment.

Application Areas

- Olefin / paraffin separations (gas and liquid mixtures)
- Phosphoric Acid
- Cumene / phenol
- p-Xylene
- Organic / water mixtures
- Acids in water
- N-paraffin / iso-paraffin

Technical Opportunities

- New, high capacity, selective, contaminant resistant, non-toxic, solvents
- Novel, low solvent inventory, contactor designs

Barriers

- Lack of selection criteria for optimum contactor configuration
- Solvent cost
- Limited solvent selectivity / capacity
- Solvent stability
- Contaminant resistant process scheme
- Solvent toxicity
- Inadequate predictive capability for solution thermodynamics (solubility, etc.)
- Emulsion and foam formation

Enabling Technologies

- Integrated process simulator to model complete hybrid process
- Predictive algorithms for solution thermodynamic
- High throughput solvent screening methods

Membrane Hybrid Systems

Research opportunities exist for membrane hybrid systems, but significant investment in membrane technology has already occurred to date. Focused research is recommended in this technical area after a detailed technical review of the economic and technical potential for implementing existing membrane systems using new design simulation tools and pilot-plant demonstrations of existing membranes where appropriate. Membranes should primarily be considered for augmenting distillation for relatively “clean” separations, such as gas recovery. Energy savings of 33% have been estimated for hybrid technologies involving membranes and distillation (Humphrey, 1991).

Pervaporation is the most widely practiced membrane-distillation hybrid system, particularly for ethanol-water separations. This is an important separation process considering the predicted rapid growth of ethanol as a fuel additive.

The use of these membrane systems is presently limited by the thermal stability and low permeation of the membrane. Higher selectivity/flux membranes that can withstand aggressive organic mixtures may be required for distillation applications for hybrid membrane systems.

Application Areas

- Azeotrope breaking (CO₂ / C₂H₆ separation)
- Pre-concentrator for distillation
- Bulk gas separations for low-temperature streams where existing polymers could be applicable
- Vent gas recovery for refining and olefin/paraffin separations
- Desalination/RO for phosphoric acid and caustic applications

Technical Opportunities

- Pilot plant demonstrations of existing materials in specific applications
- Model Predictive Control (MPC) for membrane process
- Material compatibility studies for entire systems (not just membrane materials)
- Improved membrane chemical stability
- Better scaling to reduce costs

Focused Research Opportunities

- Inorganic metal membranes: Potential opportunities include nano-structured membranes and zeolite membranes. Inorganic metallic molecular sieving membrane technology has high potential for distillation applications. These membranes also have potential use in molecular-sieving for gas-component separations, high-temperature gas-particulate separations, and a range of liquid separations. Research requirements include refinement of the fabrication process to reduce defects in large scale membranes, durability and reliability testing of the membranes, erosion and corrosion resistance of membranes under long-term test conditions, and the development of thin inorganic membrane films which will exhibit high fluxes.
- Ceramic membranes: To date, there has been no development of ceramic membranes for high-temperature applications, such as distillation. Materials that can operate with the desired selectivity and flux would need to be developed. The challenge for ceramic membranes to meet selectivity and flux criteria will be extremely high for separation of large molecules and similar size molecules.

- Polymer and composite membranes: Polymer-inorganic composite membranes that have been developed to date have been for low temperature applications. Future research should focus on the fabrication of low-cost membrane modules for high-selectivity applications, and development of composite materials that can withstand the chemical and physical environment required for distillation applications. Chemically and thermally resistant polymer membranes and composites are required for intermediate (< 250 C) temperature separations.
- Module design and engineering analysis: Efforts are needed on new module configuration designs, fouling control, and advanced control systems. A major obstacle is the high costs, particularly for high-volume applications. The cost for membranes scales linearly with size, whereas the cost per unit volume of most equipment decreases with size. Major cost reductions have been achieved in recent years for membrane systems by converting from plate and frame systems to spiral wound or hollow fiber modules. Additional advances in module design, such as learning to spin ceramic and metal membranes into fibers, will be required to produce membrane modules with high surface area at a price that is cost effective for competing with distillation.

Barriers

- High pressure drop across membrane for low pressure applications
- Solute selectivity
- Chemical, environmental, and temperature stability
- Fouling
- Limited membrane life due to membrane degradation

Enabling Technologies

- Integrated process simulator to model complete hybrid process
- Predictive membrane and module performance models

Crystallization Hybrid Systems

As shown in Table 2.1, few R&D opportunities were identified for crystallization hybrid systems in high-energy applications. However, the technology offers the potential of reducing energy requirements by taking advantage of differences in component freezing points. A good example is the separation of orthoxylene and paraxylenes. Like solvent extraction, a primary barrier is the lack of process conceptualization tools.

Application Areas

- Phosphoric acid (crystallization)
- Caustic soda – chlorine (crystallization)

- Ammonia/CO₂ recovery (absorption)
- Hydrogen (absorption)

Barriers

- Costs for replacing existing systems
- High costs of operation
- Inability to evaluate the applicability of the process for specific flow sheets

Technical Opportunities and Enabling Technologies

The R&D requirements for absorption are very similar to solvent extraction. They include:

- New, high capacity, selective, contaminant resistant, no-toxic, solvents
- Improved equipment design
- Develop process conceptualization tools for evaluation of hybrid processes

The R&D requirements for melt and freeze crystallization include

- Develop process conceptualization tools for evaluation of hybrid processes
- Develop improved solid/liquid equilibrium prediction capabilities for melt crystallization
- Develop new separation steps for freeze concentration

Cross-cutting Enabling Technologies

It must be stressed that separation technology in the chemical and petrochemical industries has become overall rather mature, which means that significant energy-reduction gains will be increasingly difficult to bring about in the future. Furthermore, the energy and overall economic savings for a separation process can be a strong function of how that process is embedded energy-wise and investment-wise into the overall process which it serves. Energy reduction calculations which are not made in the context of the overall process will be found to be misleading. These factors and the long economic life of existing facilities are deterrents to the development of economic, large-scale, non-conventional, energy-saving separation technologies to replace older processes, or to make possible new paths to products.

Therefore, it is imperative to have enabling tools that will allow industrial users and technology developers to evaluate opportunities and predict how a hybrid system will perform for a specific plant application. This tool needs to include both conceptual design and economic evaluation capabilities. The tool should be equivalent to the process simulators presently available for distillation columns.

In addition, engineering-scale pilot-plant demonstrations are needed for entire hybrid systems, including pre-feed systems and equipment configurations similar to those that

would be used in industrial applications. For a membrane system, this would require a full membrane module be tested.

Other high-priority enabling technologies include development of methods to predict non-ideal phase equilibrium, high-throughput screening tools for mass separating agents, public experimental performance databases, and molecular simulators for separations technology physics.

Technical Opportunities

- Hybrid process conceptualization/flow sheeting
- Experimental public database for adsorption
- Non-ideal liquid phase equilibrium estimation for extraction
- High-throughput screening tools for solvent and extraction equipment selection

3. Improved Distillation Equipment

Research that will lead to breakthrough technology innovations in distillation equipment design is identified below. The boundaries for the evaluation included the distillation system heat exchange and column components, such as column internals, internal heat integration, and column geometries.

Opportunities for improving equipment in existing distillation systems included divided wall columns, improved packing designs, heat integrated distillation, and improving mass transfer efficiencies. A better fundamental understanding of mass transfer, gas/liquid contact area, and multi-component data are needed to improve packing designs and mass transfer efficiencies. Independent technical reviews of existing industrial applications and pilot-plant demonstrations are needed for wide-spread implementation of divided wall columns and heat integrated distillation systems.

While most advances in distillation equipment design have been incremental, the potential exists for step changes in mass transfer and heat transfer equipment. Even small improvements in distillation column operation can produce major energy savings.

Atmospheric and vacuum distillation provide the first separation cuts of all crude oil and accounts for 35-40% of all industrial process energy consumption. Because these products contain a complex mixture of hydrocarbons and are characterized primarily by their specific boiling ranges, distillation will remain the best process for making these thermal and molecular size cuts. Therefore, little opportunity exists for replacing or augmenting atmospheric and vacuum distillation in petroleum refining. Energy-saving R&D in this area should focus on improvements to existing distillation equipment. Previous ITP studies (J.L. Humphrey, 1991) indicate that process control improvements and column internal improvements should be applicable to all existing distillation systems and could exceed one trillion BTU/yr.

The debottlenecking opportunities described above cannot be implemented generically across the industry; they will be specific to a particular process flow sheet. To overcome the market acceptance and economic barriers described below, enabling tools that will allow evaluations at the plant-specific level are critical in the implementation of these technologies. These include the development of complete process simulation packages for all candidate separations.

Technical Opportunities

- Divided wall columns
- Improved understanding of the contacting process
- Better design algorithms, especially for multi-component systems
- Reactive distillation processes

Barriers

- Conservative nature of industry, low risk tolerance
- Limited computational power
- Lack of available experimental and commercial information on divided wall column performance
- Limited modeling algorithms for novel column designs
- Lack of multi-component performance data for all column internal types
- Lack of experimental data for non-traditional physical property systems
- Lack of understanding of basic hydraulic and mass transfer physics
- Lack of truly predictive models for hydraulics and mass transfer
- Robust, longer life, catalyst systems for reactive distillation
- Catalyst replacement systems for reactive distillation columns

Enabling Technologies

- Enhanced experimental techniques to evaluate local scale mass transfer and hydraulic behavior
- Higher speed computational platforms
- Larger “open literature” experimental database
- Improved catalyst and catalytic packing geometries for reactive distillation

4. Appendices

Appendix 1. Workshop Agenda

DOE Workshop Agenda
Tuesday 2/22/05
Hybrid Technology Workshop
Pickle Research Center Commons Building

8:00 Welcome /continental breakfast / coffee

8:15 Review of current DOE programs and overview of workshop goals. *Dickson Ozokwelu*

8:45 Brainstorming session background information *Bruce Eldridge*

- Overview of high energy consuming processes identified by prior roadmaps.
- Solicitation of additional candidate processes from attendees.
- Constraints and evaluation criteria for brainstorming sessions

9:15 Break-out Sessions

Extraction / Crystallization (*Facilitator – Frank Seibert*)

Adsorption (*Facilitator – Bruce Eldridge*)

Membranes (*Facilitator – Jo Rogers*)

Sessions will identify technical opportunities and specific R&D needs for developing hybrid systems for the candidate processes. The barriers to technical and commercial success and R&D needs to overcome these barriers will be identified. The potential projects will be prioritized based on probability of technical and commercial success.

11:30 Lunch PRC Cafeteria

12:15 SRP Facility Tour

12:45 Process Presentation

During this session the three subgroups will present and discuss the candidate hybrid technologies identified during the morning break-out sessions.

1:30 Open discussion and process ranking

This session will develop a rank for the presented technologies in three distinct categories (technical feasibility, capital investment reduction, and energy savings potential).

2:45 Break

3:00 Development of prioritized research needs list

This final session will summarize R&D needs and the likelihood of commercial success for a prioritized list of hybrid technology research projects which should be considered for funding by DOE.

DOE Workshop Agenda
Wednesday 2/23/05
Distillation Technology Workshop
Pickle Research Center Commons Building Rm 1.112G

8:00 Welcome / continental breakfast / coffee

8:15 Introduction of workshop goals

Bruce Eldridge

The session will identify technical opportunities for incorporating new technologies, both hardware and software, into distillation systems for the high energy consuming processes. For purposes of this session, the distillation system is defined as the column, internals, and heat exchange components.

8:45 Identify technology R&D needs

Session will identify technical opportunities and specific R&D needs for new distillation technologies. The barriers to technical and commercial success and R&D needs to overcome the barriers will be identified. The projects will be prioritized based on probability of success for various concept groups (internals, control, column modifications etc.)

9:45 Open discussion and process ranking

This session will develop a rank for the brainstorming session concepts in three distinct categories (technical feasibility, capital investment reduction, and energy savings).

11:00 Development of prioritized research project list

This final session will summarize technology R&D needs for a prioritized list of research projects (ranked by likelihood of commercial and technical success) which should be considered for funding by DOE.

Appendix 2. Workshop Participants

Rakesh Agrawal (Purdue)
Jim Elder (Rohm & Haas)
Wayne Eng (BP)
Donald Erickson (Energy Concepts)
John Farone (Consultant)
Tim Frank (Dow Chemical)
Benny Freeman (UT-Austin)
Don Glatz (Koch MPS)
George Hayden (Mead Westvaco)
Hank Howard (Praxair)
James Kenning (Eastman)
Mike Lockett (Praxair)
Mitch Loescher (CD-Tech)
Jeffrey Logsdon (BP)
Kirk Nadler (ExxonMobil)

Behzad Nazar (BP)
Izak Nieuwoudt (KochGlitsch)
Dickson Ozokwelu (DOE)
John Pendergast (Dow)
Mark Pilling (SulzerChemtech)
Jim Ritter (USC)
Antonio Rocha (Consultant)
Ron Rousseau (Ga Tech)
Frank Rukovena (Consultant)
Ed Sanders (Air Liquide)
Frank Seibert (UT-Austin)
Paul Steacy (UOP)
Barbara Todd (ConocoPhillips)
Lisa Tung (Rohm & Haas)

Workshop Staff

Karla Bell (BCS)
Steve Briggs (UT-Austin)
Eric Chen (UT-Austin)
Bruce Eldridge (UT-Austin)
Christian Green (UT-Austin)
Chris Lewis (UT-Austin)
Leslie Pezzullo (BCS)
Sharon Robinson (ORNL)
Jo Rogers (AIChE)
Lina Rueda (UT-Austin)
Frank Seibert (UT-Austin)
Sande Storey (UT-Austin)

Appendix 3. R&D Needs for Hybrid Systems

Table A.3.1 Opportunities, Barriers, and R&D Needs for Hybrid Distillation System

Technology	Technical Opportunity	Ranking (0 - 23)	Barriers	R&D Needs
Extraction	Process Conceptualization	23	Industry is reluctant to adopt new technologies Industry is not familiar with concepts	Develop process conceptualization tools
	Phase Equilibrium	19	Existing models, i.e. UNIFAC, are not applicable to multifunctional solvents Lack of data, especially in low concentration ranges	Develop new phase equilibrium estimation tools
	High-Throughput Solvent Screening	13	Lack of screening processes increases costs and time requirements for developing new solvents	Develop high-throughput screening tools
	Mass Transport Data	13	Lack of data Existing screening methods require mini-plant operation Extractor equipment requirements for new solvents can't determined early in development process	Rapid small-scale tests for solvent mass transport data & screening extractor equipment using ~100mL of feed
Adsorption	Hybrid Process Synthesis Methodology	21	Lack of complete understanding of process synthesis Very few true broad separations experts Lack of integrated simulation capability	Interdisciplinary research Develop simulation tools
	Public Performance Data Base	20	Lack of pooled data Narrow range of data	Accumulate and pool data New thermodynamic data acquisition
	Molecular Simulation	16	Lack of computational power Lack of understanding of physics, systems, & fouling mechanisms Lack of adsorbent data, design methodology, & novel materials	Further study of physics Accurate performance estimates Fundamental research
				Interdisciplinary research Investigation of fouling and adsorbent cleaning
	Integrated Liquid Phase Adsorption	0	Capacity Regeneration	New materials with higher capacity
	Bulk Adsorption at Lower Pressure	0	Adsorption capacity Lack of understanding cycles	Develop understanding of cycles (multiple beds)
	Process Synthesis & Cycle Design	0	Lack of original cycle concepts & ideas	Combine ideas & investigate alternative cycles
	Adsorbent Structure Configuration	0	Perceived cost of development/implementation Risk Lack of demonstration	Wide scale proof of concept Develop design criteria - shapes, methodology

Table A.3.1 Opportunities, Barriers, and R&D Needs for Hybrid Distillation System Continued

Technology	Technical Opportunity	Ranking (0 - 23)	Barriers	R&D Needs
Membranes	Prefractionate Feed	19	Need high driving force	Pilot plant demonstration of existing materials in specific applications
			Need to recompress	
			Feed can be dirty	
			Ability to operate in a condensing environment	
	Debottlenecking Azetrope Breakers	17	Separation efficiency	Predictive model control
			Pressure drop across the membrane	Pilot plant demonstration of existing materials in specific applications
			Selectivity	Material compatibility for the system (not just membrane)
			Membrane that works in a liquid phase	Improve chemical stability of membrane system
			Temperature	Conceptualize PFD
			Flowsheet specific for debottlenecking	Develop models
			Lack of process simulation models for industry	Better scaling to bring down cost/ft ² (e.g. natural gas)
			Ability to operate in a condensing environment	Need technical experts
	Bulk Gas Cuts	14	Application specific; rough cut must make sense within the process	Pilot plant demonstration of existing materials in specific applications
			Cost of pre-cleaning before membrane	
			Product needs to be the residue	
			Limited economies of scale	
			Limited life	
			Turndown controls—right number of elements to manage dew point	
	Syn Gas Ratio Improvement	0	Feedstock specific	Pilot plant demonstration of existing materials in specific applications
			Newer technology	
			Replace PSA or cryogenic	
			Capital costs	
	Vent (Off-Gas) Recovery	0	Compression pressure	Pilot plant demonstration of existing materials in specific applications
Concentration				
Driving force				
Economics				
Desalination/Reverse Osmosis	0	Ability to operate in a condensing environment		
		Economics	Pilot plant demonstration of existing materials in specific applications	
		Fouling		
		Chemical stability		
		Membrane degradation		
Chemical treatment to prevent scaling/crystallization on the membrane; over the solubility limit				

Table A.3.1 Opportunities, Barriers, and R&D Needs for Hybrid Distillation System Continued

Technology	Technical Opportunity	Ranking (0 - 23)	Barriers	R&D Needs
Crystallization	Melt Crystallization	0	Para-xylene success cannot be easily evaluated for other applications	Develop process conceptualization tools
				Develop improved solid/liquid equilibrium prediction capabilities
	Freeze Concentration	0	Costs for replacing existing equipment	Develop process conceptualization tools
			High costs of solid/liquid separations & refrigeration	Develop new separations steps

Table A.3.2 High Priority R&D Needs for Hybrid Distillation Systems

R&D Need	Ranking¹	
	Overall	Technical
Hybrid Process Conceptualization/Flowsheeting (Extraction, Adsorption, Crystallization, Membranes)	28	22
Adsorption Public Database (Experimental)	16	15
Non-ideal Liquid Phase Equilibrium Estimation	14	16
High-Throughput Screening of Mass Separating Agent	14	16
Membrane Debottlenecking in Distillation	12	11
Membrane Prefractionation of Feed	10	11
Membrane Bulk Cuts	7	6
Adsorption Molecular Simulation	5	3

¹Based on workshop attendees' assessment of overall need and probability of technical success

Appendix 4. R&D Needs for Improved Equipment

Table A.4.1 Opportunities for Improved Distillation Equipment

Opportunity	Ranking ¹	
	Individual	Overall
Programmatic Opportunities		
Sharing of industry best practices on operational side (ethylene producers conference for separations energy)	17	
SRP/FRI cooperation (Best practices)	16	
DOE providing guarantee for first implementation of new technology. Was done 20 years ago – if new catalysis did not work, DOE would reimburse company	16	
Technical Opportunities		
Divided Wall Columns: Calculation methods, Perception of inflexibility versus 2- column systems, Vapor distribution sensitivity, Degrees of freedom during design	15	13
Multicomponent Practical (versus rate based) Packing Design Methodology	11	12
Mass Transfer Efficiency: Including packing	14	12
Improved fundamentals for G/L contact area	13	10
Systematic Heat integrated distillation evaluation, including economic evaluation	11	9
Foaming (unexpected)	10	8
Inert gas effect (vacuum). Need models to determine how this impacts energy considerations – major energy hog. Convergence methodology. Equilibrium efficiency. Minimum wetting	10	6
Packing – CFD modeling	11	6
Compact multi stage distillation horizontal configuration allow improvements in RR etc.	11	5
Mass Transfer Efficiency: Low concentrations (down to 1 ppm range)	11	4
Formation of two liquid phases – efficiency and hydraulics	14	2
Place to test novel prototype designs	13	1
Divided wall columns : understand dynamics	13	0
Mass transfer between multicomponent phases	12	0
Divided wall columns: Hardware - how to make it happen	11	0

Table A.4.1 Opportunities for Improved Distillation Equipment Continued

Opportunity	Ranking ¹	
	Individual	Overall
Technical Opportunities Continued		
Rate-based distillation models	9	
Study reboiler column configuration possibilities	9	
Heat pump applications study – C2/C3 Splitters only place used now	9	
Column internals that goes beyond system limitations	8	
Real-time energy optimization operating “in the zone”	8	
Process intensification – horizontal, faster, cheaper. Minimizing fixed assets	8	
Study introducing vapor to the reboiler – distribution. Liquid back to reboiler	8	
Multicomponent distillation configuration (sequencing)	7	
Extend CRD modeling to tray design	7	
Standardized design approaches for novel heat integration systems, heat pumps, etc. Need whole picture.		
Innovative designs	7	
Mass Transfer Efficiency: Low liquid rates	6	
Blended packing – one vendor marketing	6	
Extractive Distillation: efficiency deviation from models (nonvolatile)	5	
Dynamic economic strategy based on APC. Look at how disturbances affect the process/energy consideration. Using real time cost to determine control methodology	5	
How efficiency is tied to design. Standardize installation/design of column accessories	4	
Systematically identify/quantify double effect distillation column applications	4	
Reactive Distillation: method for catalytic installation	4	
Fill in data gaps for multicomponent distillation for general purpose operating tool for rate based modeling	4	
Innovative ways of heat recovery form condensers	4	
Extractive Distillation: slurry/oils. Molecular sieves. Recovery column. KTU. Xylene separation in 50 stages	4	

Table A.4.1 Opportunities for Improved Distillation Equipment Continued

Opportunity	Ranking ¹	
	Individual	Overall
Technical Opportunities Continued		
High l/v; minimum stripping	4	
Tray/packing hybrid systems	4	
Micro-channel distillation – microreactors, O2/H2	4	
Batch distillation	3	
HIGEE Evaluation	3	
HIDEC/Japanese shell in shell	3	
Systematic sequence optimization	3	
Exergy analysis - software	3	
Reactive Distillation: improved tray design for homogeneous systems	2	
LINAS Distillation	1	
Mass Transfer Efficiency: Multicomponent systems and packing interactions. Need fundamentals to prevent over design	0	

¹Based on workshop attendees' assessment of overall need and probability of technical success

Table A.4.2 High Priority R&D Needs for Improved Distillation Equipment

Opportunity	Barriers	R&D Needs
Divided Wall Columns	Lack of economic evaluation methodology	Independent review of technology and guidelines of when to use technology
	Lack of calculation methodology	Demonstration of control (dynamic modeling and experimental validation)
	Commercially available alternatives	Determine applications and energy savings (30% savings on capital/energy noted to date)
	Risk perception	
	Process risk - less flexible	
	Steady state num methods and modeling	
	Perceived operational difficulties	
	Vapor distribution	
	Demonstrations/proof of concept - half column or full column data. Several companies have operating units	
	Design tools hard to use	
	Lack of information on control. Are perceived problems real?	
	Lack of process conceptualization tools to evaluate for specific applications	
	Lack of information sharing of information by limited companies using	
	Limited applicability	
Multicomponent practical (versus rate based) packing design methodology	Lack of studies to show what would work	Develop model for packing
	Lack of data for modeling	Collect multicomponent data
	Lack of model for packing (have for trays)	
	Lack of model results in over designing and energy inefficiency	
Mass transfer efficiency (including packing)	Lack of credible modern data to use in models	Independent review of technology
	Lack of physical property data	Generate modern multicomponent data and evaluate with existing 10 models
	Small range of data with efficiencies	Perform economic evaluation
	Inconsistent use of efficiency definitions between models	
	Lack of economic evaluation of impact of lack of models/information	

Table A.4.2 High Priority R&D Needs for Improved Distillation Equipment Continued

Opportunity	Barriers	R&D Needs
Improved fundamentals for gas/liquid contact area	Lack of modern multicomponent data	Develop data for relative comparison for screening purposes
	Lack of data for nonaqueous systems	Develop of non air/water/caustic system
	Measurement of KA: gas phase/liquid phase resistance	Effect of surface tension/wetting
	Lack of experimental and model agreement	Develop fundamental understanding pf gas/liquid contact area
	Lack of liquid phase understanding	Refine experimental techniques for determining effect of liquid/gas phase resistance
	Effect of liquid viscosity, i.e. how does it spread on packing?	Understand minimum wettability - deep vacuum systems with low liquid rates
	Effect of auxiliary equipment on contactor area, i.e. distributors	Develop understanding of distributor design (liquid and vapor)