Quadrennial Technology Review 2015

Chapter 6: Innovating Clean Energy Technologies in Advanced Manufacturing

Technology Assessments

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U.S. DEPARTMENT OF ENERGY

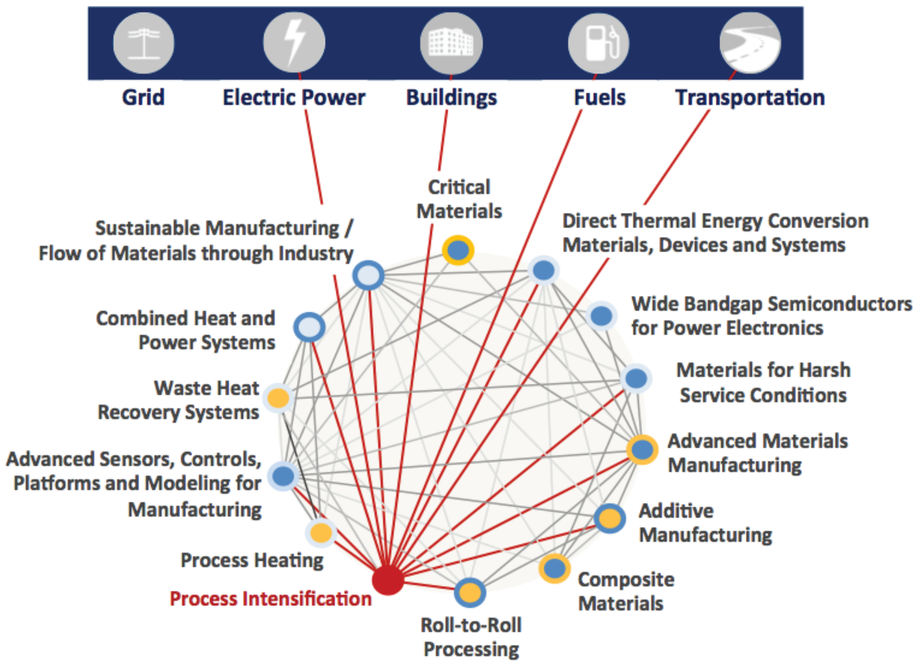
Quadrennial Technology Review 2015

Process Intensification

Chapter 6: Technology Assessments

NOTE: This technology assessment is available as an appendix to the 2015 Quadrennial Technology Review (QTR). Process Intensification is one of fourteen manufacturing-focused technology assessments prepared in support of Chapter 6: Innovating Clean Energy Technologies in Advanced Manufacturing. For context within the 2015 QTR, key connections between this technology assessment, other QTR technology chapters, and other Chapter 6 technology assessments are illustrated below.

Connections to other QTR Chapters and Technology Assessments



Representative Intra-Chapter Connections	Representative Extra-Chapter Connections
■ **Process Heating / Waste Heat Recovery:** integrated control systems; replacement of batch operations with continuous ones; facility integration to enable re-use of exhaust gases in lower-temperature processes ■ **Combined Heat and Power / Sustainable Manufacturing:** modular equipment design for easier reconfiguration, upgrade and repair ■ **Roll-to-Roll Processing:** roll-to-roll for production of separation membranes ■ **Additive Manufacturing:** microchannel reactor fabrication ■ **Advanced Sensors, Controls, Platforms, and Modeling for Manufacturing:** on-line data acquisition and modeling for process control; enterprise-wide operations optimization	■ **Fuels:** natural gas and modular production ■ **Electric Power:** chemical conversion of biofeedstocks; separations for CCS ■ **Buildings:** membranes for dehumidification ■ **Transportation:** adsorbent systems for compressed gas storage

Introduction

Process intensification (PI) targets dramatic improvements in manufacturing and processing of chemical products by rethinking existing operation schemes into ones that are both more precise and more efficient. PI frequently involves combining separate unit operations such as reaction and separation into a single piece of equipment, resulting in a more efficient, cleaner, and more economical manufacturing process. At the molecular level, PI technologies significantly enhance mixing, which improves mass and heat transfer, reaction kinetics, yields, and selectivity. These improvements translate into reductions in equipment numbers, facility footprint, and process complexity, and, thereby, minimize cost and risk in chemical manufacturing facilities.

At the core of PI is the optimization of process performance by focusing on molecular level kinetics, thermodynamics, and heat and mass transfer. Gerven and Stankiewicz provide four guiding principles for PI:[1]

- Maximize effectiveness of intramolecular and intermolecular events (example: dynamically changing conditions to attain kinetic regimes with higher conversion and selectivity).
- Provide all molecules the same process experience (example: plug flow reactor with uniform, gradient-less heating).
- Optimize driving forces at all scales and maximize the specific surface areas to which they apply (example: increase transfer surface area through microchannel designs).
- Maximize synergistic effects from partial processes (example: affecting reaction equilibrium by removing products where and when they are formed).

PI designs that achieve all or some of these molecular-level optimal conditions are likely to be transformative. Reactors that enable precise control of the reactor environment could dramatically increase yields, conversions, and selectivity, which in turn would reduce material, energy, and carbon intensities, minimize purification needs, and reduce waste disposal burdens. Additionally, PI technologies could enable the manufacture of products that otherwise could not be safely or successfully made.

Figure 6.J.1 displays a taxonomy of PI technologies informed by Stankiewicz and Moulijn.[2] PI equipment is characterized by designs that optimize mass, heat, and momentum transfer (e.g., micro-channel reactors, spinning disk reactors, static mixers, centrifugal contactors). PI methods involve integration of multiple processing steps (e.g., reactive distillation, fuel cells, membrane absorption, adsorptive distillation) and application of alternative energy sources (e.g., microwaves, electric fields, ultrasound, centrifugal fields).

Commercial applications of PI date back to the 1970s. Static mixers, which are ubiquitous today, were early PI inventions. Other early PI technologies deployed reactive distillation, including Eastman Chemical Company's tower reactor, which integrated five processing steps in the production of methyl acetate from methanol, achieving an 80% reduction in energy and a large reduction in capital cost.[3] In the petrochemical industry, reactive distillation, divided wall column (DWC) distillation, and reverse flow reactors have been commercialized each with more than 100 installations, as shown in Table 6.J.1.[4] Drivers for PI innovation include the potential for reduction in feedstock cost from improved yields, less capital expenditure from fewer pieces of equipment, and lower energy use from more efficient kinetics and heat and mass transfer. Barriers to deployment include risk of failure, scale-up unknowns, unreliability of equipment, and uncertain safety, health, and environmental impacts.

Reactive distillation is an established technology that combines the process steps of reaction and separation into a single column equipped with catalytic packing. Equilibrium-limited reactions are driven towards higher yields by separating the reactants from the products. Further, heats of reaction are applied directly to the separation process. Advantages of reactive distillation include fewer pieces of equipment, lower capital cost, lower energy use, and higher product yields (especially for equilibrium-limited reactions).

Figure 6.J.1 Taxonomy of PI Technologies[2]

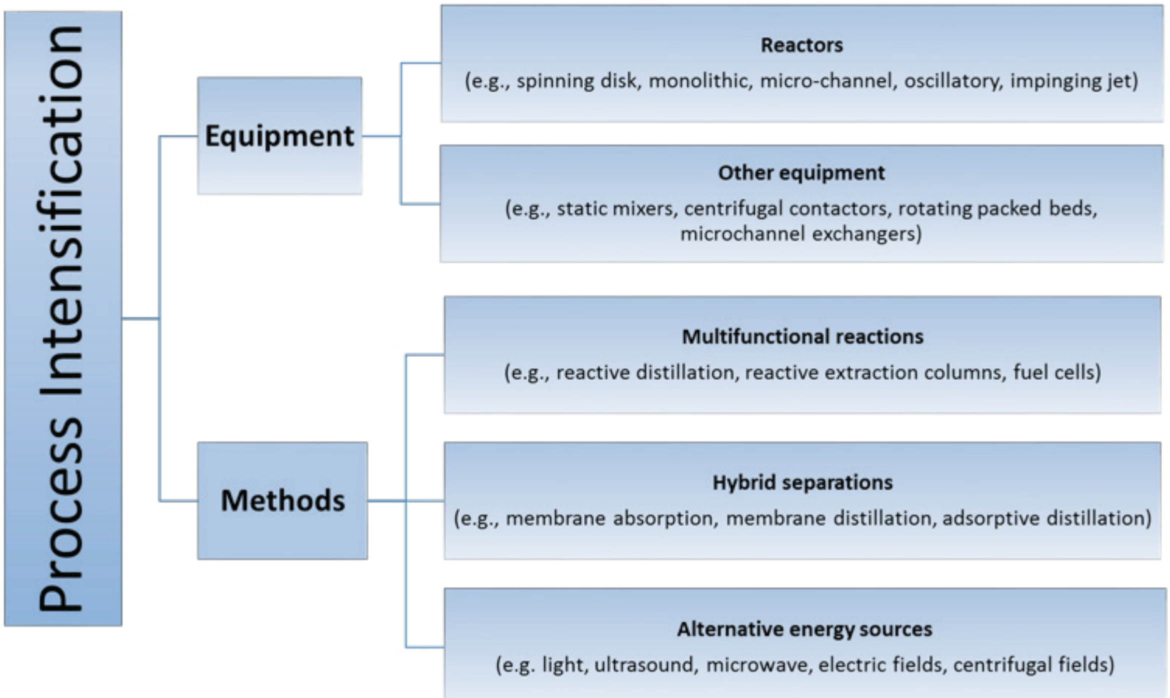


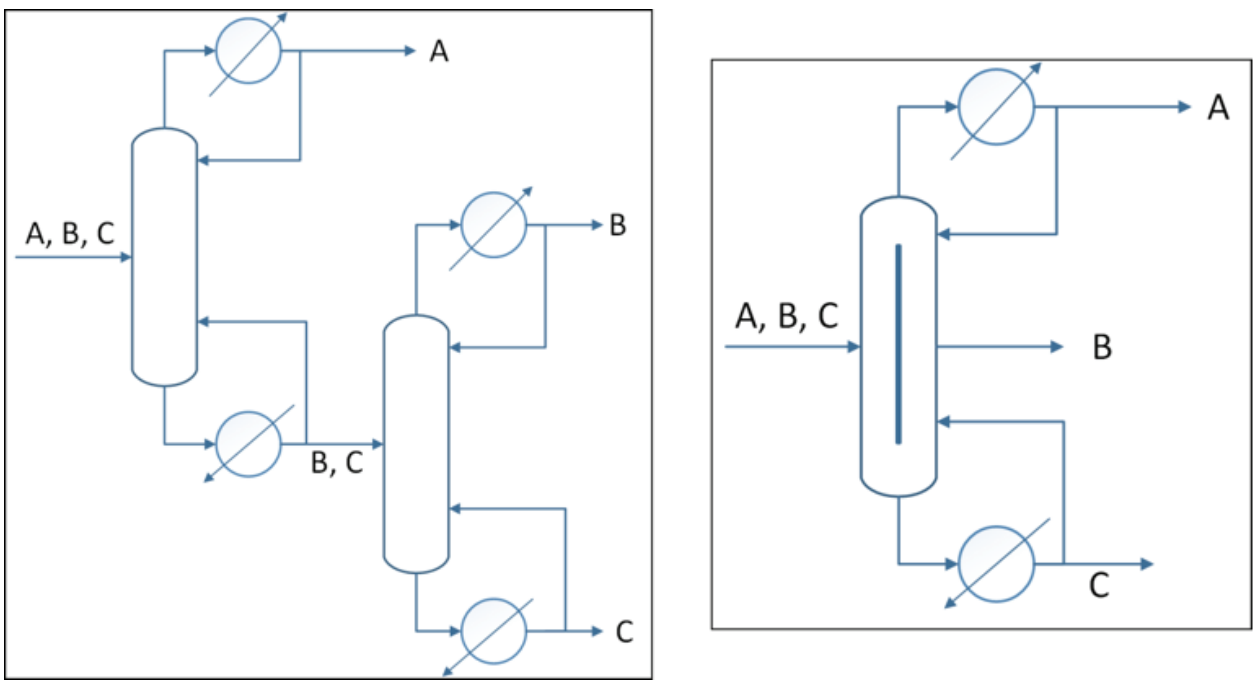
Table 6.J.1 Commercial Application of PI Technologies in the Petrochemical Industry[4]

Technology	Innovation Drivers		Commercial Implementation
	Capital cost reduction	Energy Reduction	
Reactive distillation	20–80%	20–80%	>150
DWC distillation	10–30%	10–30%	>100
Reverse flow reactor	>20%	Low	>100

Disadvantages may include complex designs, high costs of catalytic packing, and mismatch of the optimal temperature and pressure conditions for the reaction and separation operations. Commercial applications cover a wide range of reaction types, including hydrogenations, hydrodesulfurization, esterification, and etherification.[5]

Divided-wall columns are equipped with vertical partitions that allow for multiple products to be recovered from a single distillation column. As an example, assume a feed contains three chemicals—A, B, and C (with A being the most volatile and C being the least volatile of the three). In conventional designs (Figure 6.J.2, left side), two distillation columns are used for the separation. In the PI design (Figure 6.J.2, right side), the separation is accomplished in one column. The feed is introduced to one side of the column, where it is distilled into A–B and B–C fractions. On the other side, A is separated from B and recovered from the condenser, C is separated from B and recovered from the reboiler, and B is recovered from a middle point. Advantages in combining two separations into one column are lower investment costs, lower maintenance costs, and lower energy use. Disadvantages are taller columns, higher pressure drop, and the constraint of a single operating pressure.

Figure 6.J.2 Distillation Column Configurations for Separating 3 Components (Left—Conventional Two-Column Configuration; Right—Divided Wall Column)



Reverse flow reactors are fixed-bed reactors that are designed for the flow direction to be periodically reversed to integrate reaction and heat transfer. For an exothermic reaction, this flow reversal creates a heat trap in the catalytic reaction section and feed preheating from exchange with product. With this design, auto-thermal reactions can be maintained, even at very low concentrations of reactants. With this advantage, the PI technology has found commercial applications in catalytic combustion of waste gases and lean methane. The dynamic operations of reverse flow reactors could be applied to non-combustion processes, providing process improvements not possible from steady-state operations. However, challenges exist in reactor design, operation, and control, which are highly dependent on reaction kinetics.

Applications for PI technologies crosscut energy-intensive industries with opportunity space in chemicals, petroleum refining, plastics, forest products, oil and gas production, and food industries, among others. PI innovation could deliver solutions to energy security, environmental, and economic challenges in areas ranging from stranded gas recovery, carbon capture, and water treatment. Commercial endeavors in these areas include microchannel reactors for converting natural gas to fuels at the well site (see textbox: *Microchannel Reactors for Gas to Liquids*),[6] vibratory shear enhanced membrane filtration for produced water treatment,[7] and reactive media filtration for nutrient removal in waste waters.[8] PI technologies under development include novel pressure swing adsorption for upgrading lean natural gases,[9] capacitive deionization for water desalination,[10] and continuous jet hydrate reactors for continuous injection of CO_2 hydrate in the deep ocean.[11] In these application areas, where environmental regulations are the main drivers for innovation, PI approaches may prove productive.

Microchannel Reactors for Gas to Liquids

Velocys is commercializing microchannel process technology originally developed at the Pacific Northwest National Laboratory. The Department of Energy supported the microchannel reactor research that successfully developed PI technology for Fischer-Tropsch (FT) reactions, producing 20x the yield of a conventional slurry reactor. The modular reactors for steam methane reforming and FT synthesis consist of parallel arrays of microchannels with dimensions in the range of 0.1 to 5.0 mm. Smaller plant design throughputs, enabled by PI, are 15–150 million standard cubic feet per day (MSCFD) natural gas, producing 1,500 to 15,000 barrels per day (bpd) of liquid product (relative to more than 30,000 bpd for conventional FT plants). Velocys has entered a joint venture with Waste Management, NRG Energy, and Ventech Engineers for a commercial plant under construction in Oklahoma City, Oklahoma, and is expected to start up in 2016.

Modular microreactors introduce new possibilities for smaller-scale, distributed production of chemicals. Challenges in their commercialization include fabrication of the microchannel reactors, design of feed and product manifolds to distribute and control flows to and from multiple microchannels, and developing scalable designs for multiple microchannel devices integrated into chemical plants.

This technology assessment focuses on applications in the chemical industry, where PI is a key development platform for efficient chemicals production. Technology evolution in the chemical industry needs to emphasize more efficient processes for the purpose of safely reducing production cost and energy consumption. In addition, the United States is uniquely positioned to benefit from the increased access to shale gas by hydraulic fracturing, or fracking. Feedstock diversity (either through an increased use of domestic natural gas or biomass) is expected to enhance the U.S. chemical sector's competitiveness and environmental footprint. To that point, PricewaterhouseCoopers LLW (PwC)[12] predicts higher profit margins and global exports for chemicals from shale gas, particularly ethylene. PwC estimates that the cost of producing ethylene from ethane in the United States fell from just under $1,000 per ton to just over $300 per ton, accredited to the drop in energy and feedstock prices experienced over the period from 2008 to 2012.

The chemicals sector is one of the most energy-intensive of all industrial sectors, with primary energy use of approximately 4.3 quads (not including feedstocks) and combustion emissions of about 252 million metric tons of carbon dioxide equivalents in 2010.[13] A European roadmapping analysis[14] concluded that research and development (R&D) investment in PI technologies could lead to improvement in overall energy efficiency of petrochemical and bulk chemical production by 20% in 30–40 years and to a 50% reduction in costs for specialty chemicals and pharmaceuticals production in 10–15 years.

Technology Assessment and Potential

Chemical Industry Focus

In the United States, nearly 14,000 manufacturers in the chemicals industry transform raw materials into more than 70,000 compounds, which are used to produce nearly every product in use today, including plastics, paper, paints, cleaners, adhesives, pharmaceuticals, cosmetics, textiles, building materials, food packaging, appliances, and electronic devices. As shown in Figure 6.J.3, commodity chemicals produced from raw materials are converted to intermediates, which span multiple sectors of the U.S. economy in areas of textiles, safe food supply, transportation, housing, recreation, communications, and health and hygiene products and goods.[15]

Figure 6.J.4 shows the feedstock and end-use energy consumed by the top 10 energy-consuming manufacturing sectors in 2010.[17] Both the refining and bulk chemicals industries are large consumers of petroleum- and natural-gas-based feedstocks. Accelerated domestic gas and oil production, enabled by horizontal drilling and fracking of unconventional formations, has led to greater availability and reduced prices of crude oil, natural gas, and natural gas liquids (NGLs).[18] These market conditions provide a competitive advantage for the U.S. chemical industry, spurring growth in capital investment, production, and exports. The American Chemistry Council forecasts 3.2% growth in U.S. chemical output in 2015 and over 3.0% per year in 2016.[19] The American Chemistry Council reports on $153 billion in capital investment, which are either in progress or announced as of September 2015.[20] The increased investment in the industry provides the opportunity for deployment of state-of-the-art and best available technologies, which are more cost, energy, and carbon efficient than the average performance of the currently installed capacity.

Figure 6.J.5 shows feedstock energy use in the U.S. chemical industry.[22] The chemicals sector consumed 2,665 TBtu of feedstock energy in 2010. Liquefied petroleum gases (LPGs)[23] and NGLs account for 74% of the feedstock energy used, while natural gas provided 18% and other feedstocks (including fuel oil, coal, coke and breeze, and other energy feeds) provided the remainder. Of the 2,665 TBtu of feedstock energy, 85% ends up in the form of finished chemical products. The remaining 15% (400 TBtu/year) provides an opportunity window for PI solutions targeted at improving chemical reaction selectivity and process yield.

Applications of PI technologies need to be evaluated in the context both of the PI equipment or method and the specific chemistry and processes used to produce the chemical. In this technology assessment, opportunities for PI are presented for several specific applications, including energy-intensive chemicals, chemicals produced from biomass feedstocks, and separations technologies.

PI Equipment and Methods

A 2007 European roadmapping analysis[24] assessed PI technologies according to their generic potential to save energy, improve cost competitiveness, and reduce CO_2 emissions as well as their maturity and likelihood to overcome barriers to adoption. Relative judgments of high, medium, and low were made for each PI technology and each commercial value metric. The PI technologies that were deemed to have high or medium potential for energy savings are listed in Table 6.J.2. These relative, qualitative valuations are the product of a team of experts and reflect their experience and judgment at the time of the assessment (i.e., 2007). Our objective in presenting their opinions is to highlight PI equipment and methods that, if developed and deployed, could yield energy savings in the chemical sector.

Figure 6.J.3 Chemical Manufacturing Pathways[16]

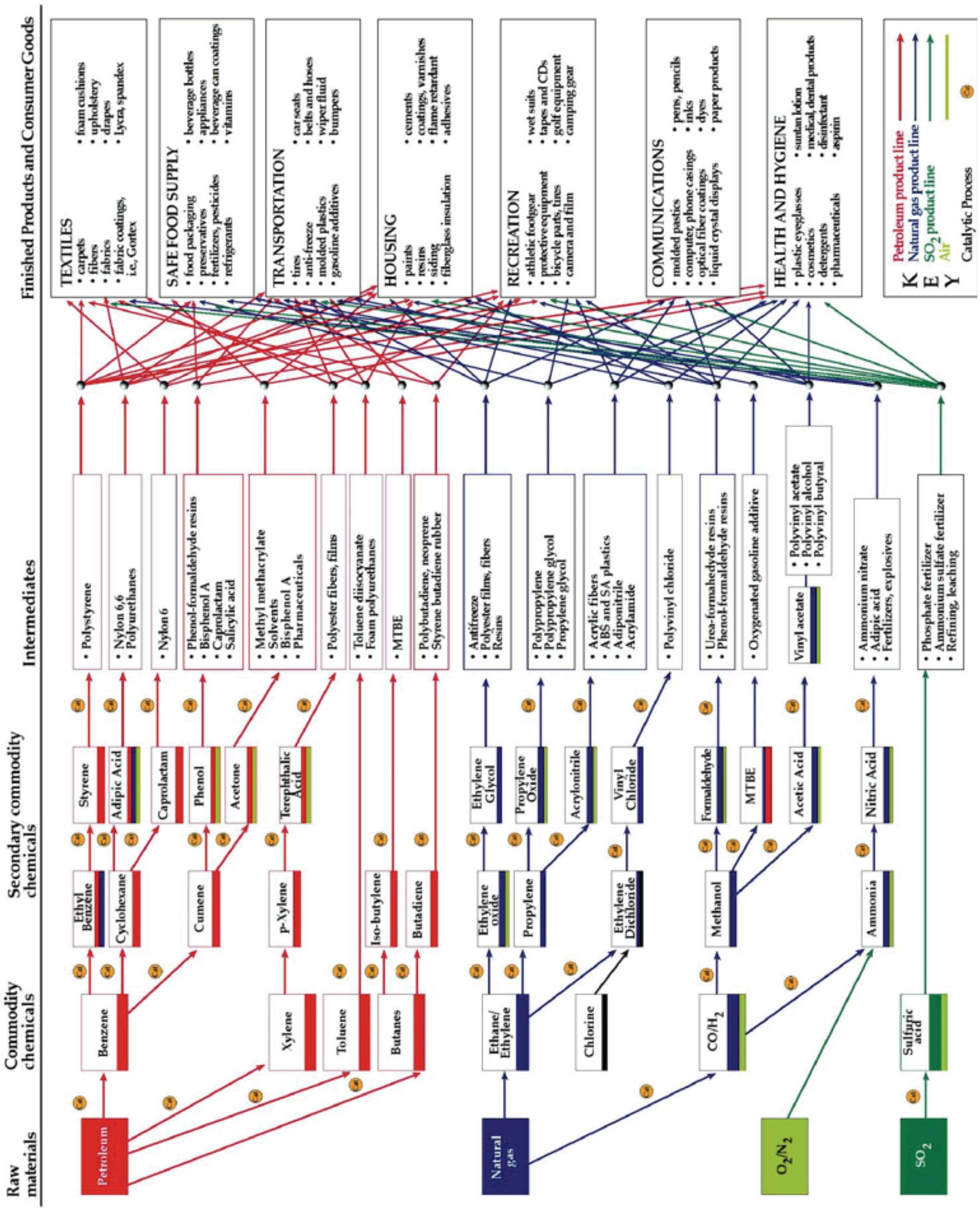


Figure 6.J.4 Top 10 Energy-Consuming Manufacturing Sectors—Energy Consumed in 2010[21]

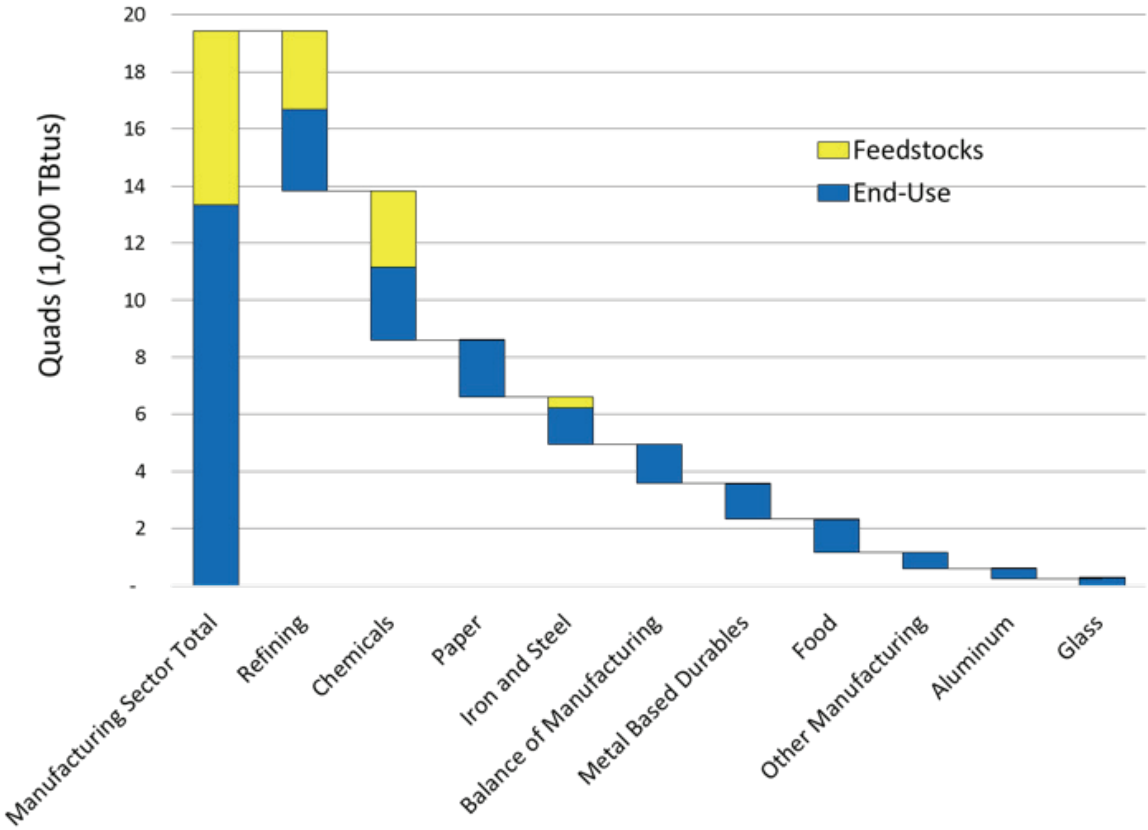


Figure 6.J.5 Feedstock Energy Consumption in the Chemical Sector (2010)[21]

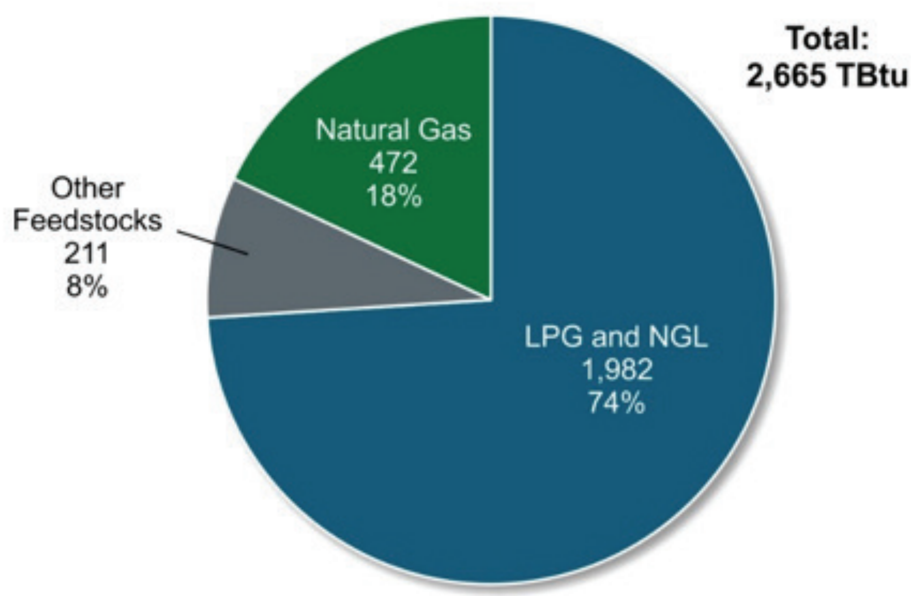


Table 6.J.2 PI Technologies with High and Medium Potential for Energy Savings as Assessed in the 2007 "European Roadmap for Process Intensification."[24] Qualitative assessment of relative merit for select PI technologies, based on expert elicitation.

PI Equipment or Method	Potential for energy savings	Potential to improve cost competitiveness	Potential to reduce CO_2	Maturity of technology	Likeliness of overcoming barriers
Heat-integrated distillation*	high	high	high	high	high
Reactive distillation	high	high	high	high	high
Membrane-assisted reactive distillation	high	high	high	high	medium
Microwave heating/microwave drying	high	high	low	high	high
Static mixer reactors for continuous reactions	high	medium	high	high	high
Pulsed compression reactor	high	medium	high	low	low
Centrifugal liquid-liquid contractors	high	medium	medium	high	high
Rotor stator devices	high	medium	medium	high	high
Photochemical	high	medium	medium	medium	medium
Reactive absorption	high	low	high	high	high
Electric field-enhanced extraction	high	low	low	high	high
Supercritical separations	medium	high	high	medium	high
Advanced Plate-type heat exchangers	medium	high	medium	high	high
Rotating packed beds	medium	high	medium	high	medium
Oscillatory	medium	high	low	high	high
Reverse flow reactor operations	medium	medium	high	medium	high
Advanced shell & tube type heat exchangers	medium	medium	medium	high	high
Static mixers	medium	medium	medium	medium	medium
Monolithic reactors	medium	medium	medium	high	high
Structured reactors	medium	medium	medium	medium	medium
Membrane crystallization technology	medium	medium	medium	low	low
Membrane distillation technology	medium	medium	medium	medium	medium
Distillation-pervaporization	medium	medium	medium	high	medium
Ultrasound reactors for enhanced mass transfer	medium	medium	medium	high	high
Hydrodynamic cavitation reactors	medium	medium	low	medium	medium

*Note: Heat-integrated distillation refers to both dividing-wall columns and heat-integrated distillation columns.

Table 6.J.2 PI Technologies with High and Medium Potential for Energy Savings as Assessed in the 2007 "European Roadmap for Process Intensification."[24] Qualitative assessment of relative merit for select PI technologies, based on expert elicitation. Continued.

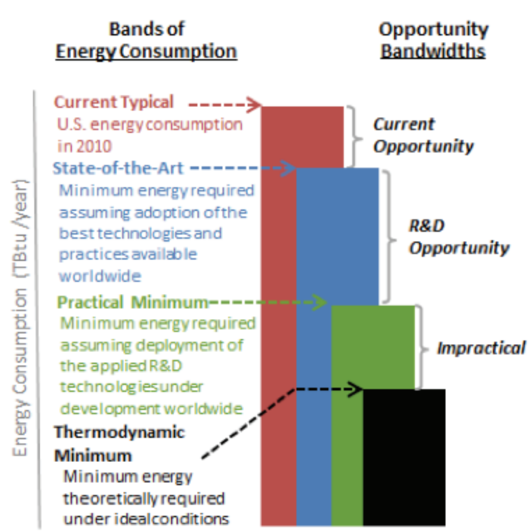
PI Equipment or Method	Potential for energy savings	Potential to improve cost competitiveness	Potential to reduce CO_2	Maturity of technology	Likeliness of overcoming barriers
Impinging streams reactor	medium	medium	low	high	medium
Sonochemical reactors	medium	medium	low	medium	medium
Ultrasound enhanced crystallization	medium	medium	low	low	low
Pulse combustion drying	medium	medium	low	low	medium
Adsorptive distillation	medium	low	medium	low	low
Reactice extraction columns, HT and HS	medium	low	medium	medium	high
Extractive distillation	medium	low	low	medium	medium

PI Technologies for Selected Energy Consuming Chemicals

The 2006 *Chemical Bandwidth Study*[25] and the 2015 *Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S Chemical Manufacturing*[21] identified some of the top energy-consuming chemicals in the United States. The Department of Energy (DOE) bandwidth studies are undertaken to quantify the energy reduction opportunities within a specific industry sector. As depicted in Figure 6.J.6, four energy bands are evaluated in these studies:

- Current typical (CT)—energy consumption in 2010
- State of the art—energy consumption reflective of existing best technologies and practices available worldwide
- Practical minimum (PM)—energy consumption that may be possible if applied R&D technologies under development worldwide are deployed
- Thermodynamic minimum—least amount of energy required under ideal conditions, typically not attainable in commercial applications

Figure 6.J.6 Energy Consumption Bands and Opportunity Bandwidths Assessed in the 2015 Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S. Chemical Manufacturing[22]



The energy differential between the CT and PM energy consumptions provides one estimate of the opportunity window for energy reduction achievable through the implementation of alternative technologies. The chemical bandwidth study provides these estimates, both for subsectors of the chemical industry and for individual energy-intensive chemicals. In this assessment, the energy differential between the CT and PM energy consumptions for an individual chemical is used as a measure of the potential energy reduction that could be achieved from widespread commercialization of PI technologies (and full development of future opportunity) in the domestic production of the chemical.

As part of an ongoing DOE study,[26] 11 chemicals have been identified to have significant opportunity for energy savings via the implementation of PI technologies: ethylene, ethanol, chlorine/sodium hydroxide, ammonia, nitrogen/oxygen, ethylene chloride, propylene, benzene, ethylene oxide, methanol, and acetone.

PI technologies being developed for ethylene production are described later in this section. Many of these technologies are also applicable to propylene production. PI options proposed for ethanol production are described below. Innovative water-gas-shift reactors, including microchannel reactors[27] and integrated membrane reactors,[28] are under development for hydrogen production from methane. These PI technologies are directly applicable to the manufacture of ammonia and methanol, for which hydrogen is a chemical reactant, and often produced on site via steam reforming of methane. In the coproduction of chlorine and sodium hydroxide, the integration of fuel cells that convert by-product hydrogen to electricity is gaining attention as a means to recover productive energy from hydrogen that is currently vented.[29]

The application of membrane technologies for the separation of nitrogen and oxygen from air is an active area of research.[30] PI technologies are being developed to meet industry-specific requirements for oxygen reactants (for example, dense inorganic ion transport membranes being developed for high temperature applications).[31] The production of benzene, acetone, ethylene oxide, and ethylene dichloride involve energy-intensive separations, for which PI technologies may be substituted. For example, sensitivity analysis of heat-integrated distillation for the benzene-toluene-xylene separation suggested the PI approach could reduce energy consumption for the separation by 30%.[32] The PI technologies described in this paragraph are only a sampling of those being explored within the research community for production of the 11 chemicals.

In 2010, the production processes for the 11 chemicals utilized 1,374 TBtu/year of on-site energy as shown in Table 6.J.3, accounting for 43% of the total on-site energy consumed in the chemicals industry. Table 6.J.3 also shows estimates of the energy reduction opportunity window (current and future opportunities, as previously defined) for each of these chemicals. The successful development and implementation of PI technologies for each of the chemicals could yield total energy savings as high as 695 TBtu/year.[33] Using a simplified assumption of $13.09/MMBtu[34] for industrial energy, these savings equate to a potential annual cost of production (COP) savings of $9.1 billion.

Globally, ammonia is the largest volume chemical produced and consumes the most energy, followed by ethylene.[35] In the United States, ethylene production consumes the most energy of all chemicals manufactured domestically. Ethylene is produced primarily from steam cracking of ethane and other NGL alkanes (e.g., propane and butanes). The supply of ethane in the United States has increased significantly in concert with increasing production of shale gas, which typically has a higher concentration of NGL than conventional natural gas. In response, several chemical companies have announced plans to increase existing or build new ethylene capacity totaling 10 million metric tons/year by 2017, which would increase the U.S. capacity by over 35%.[36] Consequently, ethylene is an important focus area for PI innovation. Table 6.J.4 shows an assessment of PI

Table 6.J.3 2010 Production, Energy Consumption, Cost of Production, and Energy Savings Potential for 11 Chemicals[27]

Chemical	Production ($1x10^6$ lbs)	Calculated Site Energy (TBtu/yr)	Energy Reduction Opportunity (TBtu/yr)	COP $/ lb	Total COP ($MM)	Savings $ / lb	Total Savings Opportunity ($MM)
Ethanol	66,080	307	264	0.061	4,019	0.052	3,456
Ethylene	52,864	374	107	0.093	4,896	0.026	1,401
Ammonia	22,691	133	78	0.077	1,741	0.045	1,021
Benzene	13,274	104	67	0.103	1,361	0.066	877
Chlorine/ Sodium Hydroxide	21,465/ 16,581	203	87	0.070	2,657	0.030	1,139
Nitrogen/ Oxygen	69,609/ 58,287	99	18	0.010	1,296	0.002	236
Ethylene Dichloride	19,426	66	37	0.044	864	0.025	484
Acetone	3,178	25	18	0.103	327	0.074	236
Propylene	31,057	42	11	0.018	550	0.005	144
Ethylene Oxide	5,876	11	4	0.025	144	0.009	52
Methanol	2,024	10	4	0.065	131	0.026	52
TOTAL	**382,412**	**1,374**	**695**		**$17,986**		**$9,098**

technologies in the pipeline for the production of ethylene along six weighting factors: technology readiness, market impact, relative cost, technical risk, productivity gain, and environmental impacts. Each technology's weighting factor is scored (as in the top table) to represent the technology's attributes along the factors. Table 6.J.4 also provides each technology's overall importance rating, derived from the six weighting factors score as described in the bottom table. The overall importance factor is the sum of the weighting factor values (1, 2, or 3) divided by the maximum sum possible (i.e., 6 factors with maximum score of 3 = 18).

Other PI approaches proposed for ethylene production include membrane reactors[37,38] and microchannel reactors[39,40] for producing ethylene from the catalytic ethane oxidative dehydrogenation pathway; microchannel reactors for catalytic dehydration of bioethanol to ethylene;[41] and reactive absorption[42,43] and adsorption with metal organic frameworks (MOFs)[44,45] for ethane/ethylene separations.

Given the energy intensity of steam cracking, PI approaches to this process step could lead to significant energy savings. Microwave-enhanced cracking of hydrocarbons is a new method for replacing energy-intensive cracking furnaces. In a conventional furnace, heat is transferred through the outer surface of coils or tubes. Microwave-enhanced cracking technology takes advantage of microwaves, which impart energy directly to the reactants, and is expected to save 30%–50% of furnace energy consumption in the cracking process step.[48,49] Another promising PI technology is catalyst-assisted production of olefins, (see textbox: *Catalytic Surface Coatings*), which provides a potential solution to downtime and efficiency losses caused by coking of the furnace walls.

Table 6.J.4 PI Technologies Applicable to the Production of Ethylene[46]

PI Technologies for Ethylene	Estimated Energy Savings (% Saving over Current Average)	Technology Readiness	Market Impact	Relative Cost	Technical Risk	Productivity Gain	Environmental Benefits	Overall Importance Rating
Microwave-Enhanced Direct Cracking of Hydrocarbon Feedstock	26%	2	3	3	2	3	3	16÷18 = 89%
Catalyst-Assisted Production of Olefins	6%–10%	2	3	2	2	2	2	13÷18 = 72%
Heat Integrated Distillation Through Use of Microchannel Technology	3.5%	2	1	1	1	1	1	7÷18 = 39%
Hollow Fiber Membranes for Olefin/ Paraffin Distillation	3%	1	2	2	2	2	2	11÷18 = 61%

	Weighting Factor Descriptions
Technology Readiness Level (TRL)[47]	1 = TRL 1–3 2 = TRL 4–6 3 = TRL 7–9
Market Impact	1 = applicable to select few establishments or unique process 2 = applicable to many establishments 3 = widely applicable to all establishments
Relative Costs	1 = implementation cost >90% of reference technology, or payback >10 years 2 = cost <90% and >40% of reference technology, payback <10 years 3 = cost <40% of reference, payback <2 years
Technical Risk	1 = low likelihood of success, multiple and significant risk factors 2 = insufficient evidence of technology success, some risk factors 3 = high likelihood of technology success and deployment, minimal risk factors
Productivity Gain	1 = no gain in productivity 2 = moderate gain in productivity 3 = significant gain in productivity, either quantity or quality of product produced
Environmental Benefits	1 = little or no environmental benefit 2 = some environmental benefits 3 = multiple and significant environmental benefits

Catalytic Surface Coatings

In the steam cracking furnace, carbonaceous materials (coke) are produced as a by-product in the process and deposit on the internal surfaces of the coils. These coke deposits cause a number of undesirable side effects, including constricting the flow of ethylene through the furnace, forcing higher furnace temperatures to maintain performance, and eventually requiring plant downtime to remove coke from the furnace walls. BASF is marketing the CAMOLTM technology, which applies an advanced coating to the inner surface of the tube and coils. The catalytic coating surface is inert to filamentous coke and gasifies amorphous coke, thereby reducing coke buildup. With this technology, the run-length of the furnace can be extended, and its heat transfer can be improved. LyondellBasell, BASF, Qtech Solutions Inc., and Quantiam® Technologies Inc. are working on developing CAMOL technology specifically for ethane cracking, with claims that 6%–10% energy reduction can be achieved.

PI efforts that focus on similarities between chemical processes will result in energy savings, cost reductions, and process improvements that will have a significant impact on the chemicals industry.

Table 6.J.5 highlights the common unit operations amongst the 11 targeted chemicals. Many of these unit operations are also employed in other industrial sectors, so the PI technologies would have broad crosscutting applicability. PI approaches that optimize energy recovery through process integration may be particularly impactful.

PI Technologies for Bio-based Chemicals

An important strategy for reducing the carbon footprint of the chemical industry is to manufacture chemicals from biomass instead of petroleum or natural gas feedstocks. To encompass this application area, the term "biorefinery" is used as defined by the National Renewable Energy Laboratory to be "a facility that integrates conversion biomass processes and equipment to produce fuels, power, and chemicals from biomass."[51]

In one account, researchers[52] foresee a future where 30% by weight of chemicals is produced from biomass by 2050 and postulate wide adoption of PI technologies within the new bio-based chemical industry. The potential for these technologies was explored by evaluating the benefits and challenges in several case studies. Results from this analysis are reprinted in Table 6.J.6. Among the PI technologies considered in their case studies are the following:

- Reactive distillation for the hydrogenation of lactic acid coupled with the removal of water
- Microchannel reactor for shifting CO with steam to produce hydrogen and CO_2
- Microwave pyrolysis of biomass in CO_2 with simultaneous supercritical fluid extraction

A recent paper[53] reviews a wide range of membrane technologies under development for the "bioeconomy." Among the novel PI technologies described are membrane bioreactors for the production of ethanol, methane, hydrogen, acetic acid, and biodiesel. One example of an innovative membrane process, developed through a DOE-sponsored program, is highlighted in textbox: *Resin Wafer Electrodionization*. Polymeric, ceramic, and hybrid membrane technologies are also being developed for the recovery of both chemical feedstocks from biomass and chemical products from mixed-process streams. The processes reviewed in the paper have shown promising performance in laboratory and pilot experiments, though many of the applications are challenged by membrane fouling. Anaerobic membrane bioreactor technology was called out as particularly attractive for wastewater treatment, having been shown to require less energy and produce higher value effluents than other processes.

Table 6.J.5 Current Process and Key Unit Operation Commonalities of 11 Chemicals[50]

Chemical	Process Conditions			Crosscutting Unit Operations						
	Cryogenic Temperatures ≤0 °C	High Temperature Reaction ≥600 °C	High Pressures ≥30 bars	Exothermic Unit Operations Present	Catalysis	Compression/ Refrigeration	Cryogenic Fractionation	Fractional Distillation	Pressure Swing Adsorption	Other Non-Distillation Separations/Purification
Ethylene	✓	✓	✓		✓	✓	✓	✓	✓	
Ethanol			✓	✓	✓			✓	✓	
Chlorine/ Sodium Hydroxide	✓					✓				✓
Ammonia		✓	✓	✓	✓	✓			✓	✓
Nitrogen/ Oxygen	✓					✓	✓		✓	
Ethylene Dichloride				✓	✓	✓		✓		✓
Propylene		✓			✓	✓		✓	✓	✓
Benzene			✓		✓			✓		
Ethylene Oxide			✓	✓	✓	✓		✓		
Methanol		✓	✓	✓	✓	✓		✓		
Acetone					✓			✓		✓

In biomass to ethanol plants, two separation challenges provide opportunity space for PI technologies.[57] First, fermentation inhibitors need to be removed from the lignocellulosic feed after the hemicelluloses have been extracted. PI technologies being developed for this detoxification step include extractive fermentation, membrane pervaporation bioreactor, and vacuum membrane distillation bioreactor.

Recovery of the fuel-grade ethanol from water is the second separation challenge. This separation is energy intensive because of the low starting concentration of ethanol (5–12 wt% ethanol) and the water-ethanol azeotrope that forms at 96.5 wt% ethanol concentration. The separation is typically undertaken in two processing steps: conventional distillation to concentrate the solution to 80–85 mol% ethanol followed by extractive or azeotropic distillation for dehydration. Novel low-energy intensive technologies under development include extractive distillation with ionic liquids or hyperbranched polymers.[57] Other energy-efficient technologies, including pervaporation and molecular sieve absorption, have been found to be constrained to low-capacity applications.[58] Evaluating a PI approach by using Aspen Plus simulations, researchers estimate energy savings of 10%–20% could be achieved by replacing an optimized two-column

Table 6.J.6 Assessment of PI Technologies* in the Manufacture of Chemicals from Biomass[52]

	Low capital	Efficient use of biomass/ fossil	Safe	Compact/ simple plant	Full use of biomass	Low transportation cost	Specific challenges
Technologies							
Electrodialysis	+	+ +	+	+	-	+	E F
Microwave/CO_2 combination	+	+	+	+	-	+	E F
Chemicals							
Propyleneglycol	+	+	+	+	-	-	E
H_2	--	--	-	-	+ +	-	A B C D F G
Cyanophicin	+ +	+ +	+ +	+	-	+ +	E F H
Isorsorbide	+ +	+ +	+ +	+ +	-	+	A B C E F
Hydroxymethyl furfural	+	+	+	+	-	+	A B E G

* + means attractive; - means not attractive
A. Separation of components from biomass at low cost and low energy use
B. Reduction of the logistic costs
C. Separations and logistics that can efficiently be performed at small scale
D. Management of toxic production formation and trace elements (e.g., S, N, P, K)
E. Identification of platform chemicals that can be produced at high volumes, yields, and efficiency
F. Sustainable approach for producing base chemicals from biomass
G. Combination of separation and conversion to minimize costs and waste streams
H. Treatment of dilute water waste streams

extractive distillation with a single DWC or 20% savings by replacing an optimized two-column azeotropic distillation with a single DWC.[59] They note that reported energy savings of 25%–40% from other studies are based on comparisons of the PI alternatives with non-optimized two column designs.

PI technologies are also being explored to reduce the residence times, operating costs, and energy consumption of producing biodiesel via transesterification of vegetable oils and animal fats. A recent review article[60] describes experimental and commercial PI technologies. Table 6.J.7 provides comparative information on the performance of these PI technologies. In general, these technologies improve production efficiency and reduce operating costs by increasing the rate of reaction through intensified transport processes and mixing of the alcohol and oil reactants. Very high-energy efficiencies have been achieved in cavitational and microwave reactors. Centrifugal contactor technology, originally developed through DOE-sponsored research on the selective recovery of metal elements from spent nuclear fuel, has been successfully applied to biodiesel production. In this continuous process, the centrifugal contactor equipment hosts both the reaction of triglycerides with alcohol and the separation of product biodiesel from by-product glycerol, achieving efficient mixing and precisely controlled residence times.[61]

PI Technologies for Separations

One crosscutting area in which PI technologies could be particularly impactful is in separations. Separation technologies are estimated to consume about 22% of in-plant energy use in the U.S. industrial sector.[62] As shown in Figure 6.J.8, separation energy-intensive manufacturing industries include chemicals, petroleum refining, and forest products.

Resin Wafer Electrodionization

Electrodeionization (EDI) is a modified version of electrodialysis (ED) that contains conductive ion exchange (IX) resin beads within the diluate compartment. EDI combines the advantages of ED and IX chromatography; however, it utilizes in-situ regeneration of the IX resin beads by a phenomenon known as "water splitting." Water splitting on the surface of the IX resin beads regenerates the beads and ensures higher ionic conductivity within the diluate compartment. EDI outperforms ED with dilute solutions, where owing to the limited ion concentration, ionic conductivity decreases and electrical energy is wasted in water splitting. In contrast, the conductive IX resin beads in EDI provide sufficient ionic conductivity, even with a dilute solution, and provide an efficient ion transport pathway through the IX resin beads. In conventional EDI, loose IX resin beads are used; however, researchers at Argonne National Laboratory have improved the technology by using resin wafers to incorporate the loose ion exchange resin, as shown in Figure 6.J.7.[54,55] The technology offers enhanced fluid and flow distribution, higher conductivity, superior pH control, ease of materials handling and system assembly, and a porous solid support for incorporation of catalysts, biocatalysts, and other adjuvants. Resin-wafer EDI is used for production and recovery of bio-based chemicals, especially organic acids from fermentation broth, post-transesterification glycerin desalting, conditioning of biomass hydrolysate liquor, and for CO_2 capture from flue gas.

Figure 6.J.7 Schematic of Resin Wafer EDI Configuration and Process Streams[56]

Credit: Argonne National Laboratory

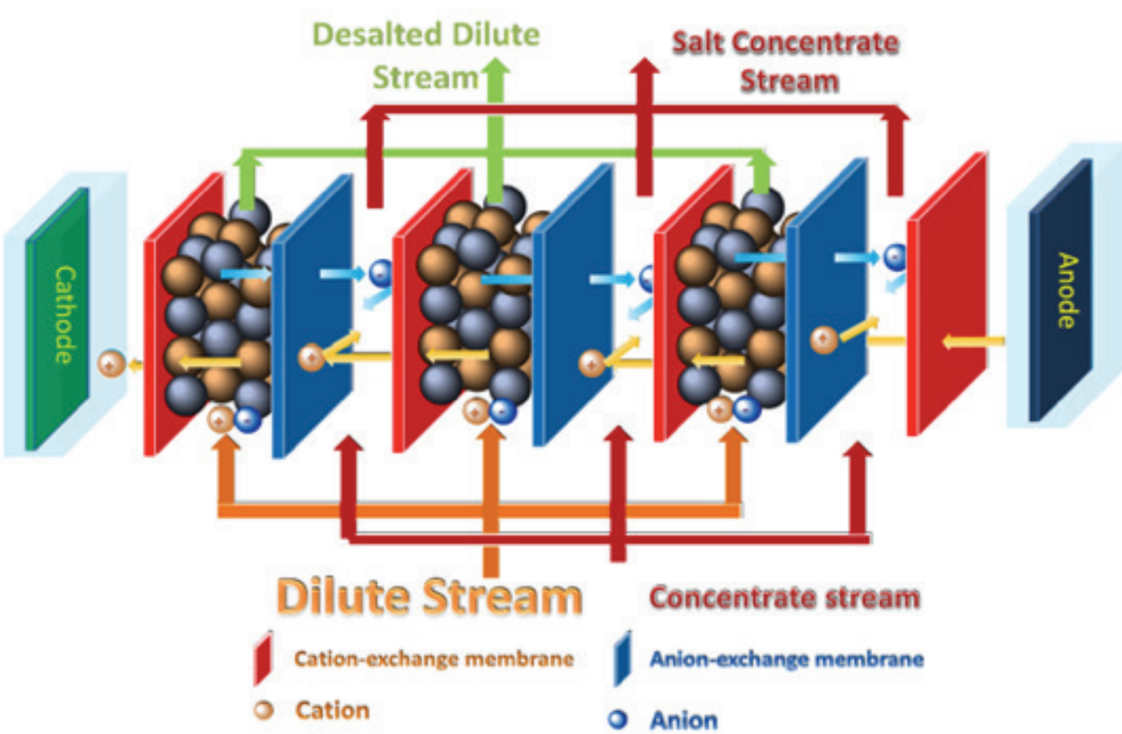


Table 6.J.7 PI Technologies for the Production of Biodiesel from Vegetable Oils and Animal Fats[59]

	Residence time	Operating and capital cost	Temperature control	Current Status
Static mixer	~30 min	Low	Good	Lab scale
Micro-channel reactor	28s to several minutes	Low	Good	Lab scale
Oscillatory flow reactor	30 min	Low	Good	Pilot plant
Cavitational reactor	Microseconds to several seconds	Low	Good	Commercial scale
Spinning tube in tube reactor	<1 min	Low	Good	Commercial scale
Microwave reactor	Several minutes	Low	Good	Lab scale
Membrane reactor	1–3 h	Lower	Easy	Pilot plant
Reactive distillation	Several minutes	Lower	Easy	Pilot plant
Centrifugal contactor	~1 min	Lower	Easy	Commercial scale

NOTE: "Low" operating and capital cost indicates reduced costs relative to traditional processes, "Lower" indicates reduced costs relative to other PI technologies. "Good" and "Easy" temperature control reflect the demonstrated capability to maintain operations at desired temperatures, enabled by efficient heat transfer.

Many types of separation technologies are currently used in industry, falling broadly into the categories of distillation, drying, evaporation, extraction, adsorption, pervaporation, membranes, crystallization, and physical separations (e.g., flotation, screening, magnetic separation). Distillation, drying, and evaporation are high-energy intensive processes, accounting for 49%, 20%, and 11%, respectively, of industrial separations energy use.[63]

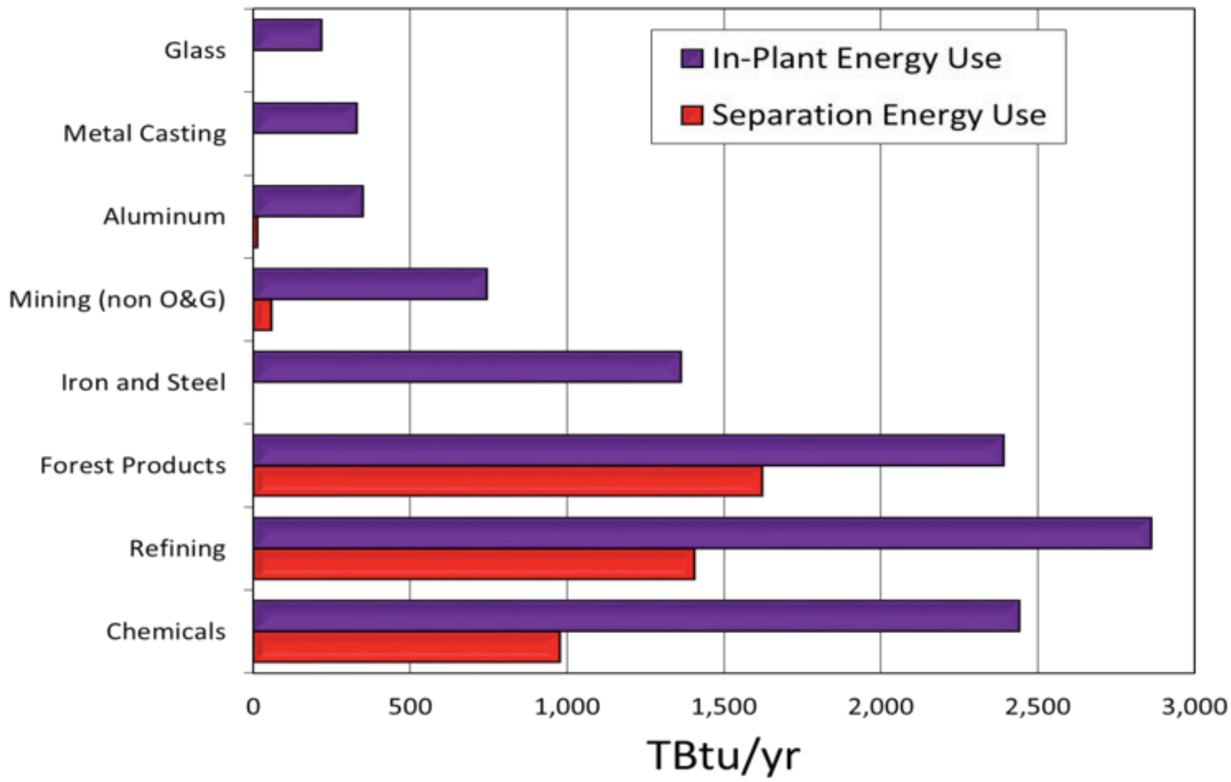
Materials and process development strategies for reducing separation energy include the following:

- Replacing high-energy intensive technologies (e.g., distillation, drying, and evaporation) with low-energy intensive technologies (e.g., extraction, absorption, adsorption, membrane separations, crystallization, and physical-property based operations)
- Adopting PI strategies (e.g., hybrid separations, reactive separations, membrane processes, and alternative energy sources—centrifugal field, ultrasound, microwave, electric fields, microwave)

A study[63] of separation applications in petroleum refining and 10 chemical processes identified several high-energy distillations, which could yield energy savings if replaced with membrane separations, extraction, absorption, and hybrid systems as follows:

- Separation of olefin-paraffin streams (e.g., ethylene/ethane, propylene/propane, butadiene/butanes, and styrene/ethylbenzene)
- Recovery of organics that azeotrope with water from aqueous solutions (e.g., ethanol, isopropanol, butanol)
- Recovery of dilute organics from dilute water solutions (e.g. acetic acid, ethylene glycol, methanol)
- Cryogenic air separation
- Polyol separations (e.g., ethylene glycol/propylene glycol, ethylene glycol/diethylene glycol)
- Isomer separations (e.g., p-xylene/mixed xylenes, n-paraffins from isoparaffins)

Figure 6.J.8 In-plant and Separation Energy Use for Energy-Intensive Industries[63]



The study also identified an energy savings opportunity for developing membrane separations to replace evaporation processes in the production of caustic soda and phosphoric acid. Table 6.J.8 provides a summary of the energy savings estimated to be possible if more energy-efficient separations technologies, including PI technologies, are deployed in these select chemical processes. Membrane separations, in particular, are commonly considered to be PI technologies because of their potential to save energy and their capability to selectively and efficiently transport specific components.[64]

Program Considerations to Support Research, Development, and Demonstration

Although a promising approach for increasing the energy, carbon, and cost efficiency of chemical processes, PI for many potential applications is in the early stages of technology readiness. Therefore, research, development, and demonstration (RD&D) investment in PI technologies is expected to be impactful and to have wide-ranging applicability across the chemical industry as well as other industries. Metrics of successful PI RD&D will encompass cost reduction, energy efficiency, carbon efficiency, and waste reduction compared to state-of-the-art technologies. An overarching goal is to apply PI methods to develop smaller, modular equipment, which has the potential to reduce waste, energy use, and capital and operating costs when compared with the existing state-of-the-art processes. Key focal areas for RD&D are as follows:

- PI equipment, involving improved physical hardware and optimized operating parameters for improved chemicals processing environments and profiles, such as novel mixing, heat-transfer, and mass-transfer technologies

Table 6.J.8 Energy Savings Potential for New Separation Technologies, Including PI Technologies[65]

Chemical Process	Separations energy (% of total energy)	Potential energy saved with new separation technology (% of separations energy)
Ethylene	24%	46%
Ammonia	25%	30%
Styrene/ethylbenzene	20%	25%
Phenol/cumene	16%	27%
Methanol	20%	20%
Phosphoric acid	25%	12%
Caustic soda	50%	2%
Nitrogen/oxygen	100%	22%

- PI methods, including improved or novel chemical processes (e.g., new or hybrid separations, integration of reaction and separation steps, improved heat exchange) or phase transition (multifunctional reactors), the use of a variety of energy sources (light, ultrasound, magnetic fields), and new process-control methods (intentional non-equilibrium-state operation)
- PI supporting practices, such as improved manufacturing processes for new equipment and improved systems integration, common standards and interoperability, modular systems design and integration, supply chain development and flexibility, workforce training, and financing

Catalysis research is integral to both PI and advanced materials manufacturing.[66] At the core of many PI approaches are hybrid reactors, which require multifunctional catalysts with specialized composition and structure. These catalysts determine the efficiency, yield, and selectivity that can be achieved in hybrid reaction and separation systems. MOFs, novel gold catalysts, and tuned mesoporous catalysts are among new types of catalysts being explored for PI applications.[67]

Advances in the RD&D agenda for advanced sensors, control, platforms, and modeling for manufacturing[68] will benefit PI technologies and deployment. Intersection points of this RD&D agenda include on-line data acquisition and modeling for robust process control, interconnection of manufacturing data with advanced computer simulation and modeling, cost-effective production of instrumentation, and enterprise-wide optimization of operations.

An important RD&D goal for PI is to provide low-energy alternatives to replace energy-intensive distillation and evaporation process steps. Many of these PI solutions require separation agents, for example, solvents, sorbents, ion exchange resins, molecular sieves, and membranes. These agents need to be developed specifically for each application because separation efficiencies depend on the chemical and physical interactions between the separation agent and the components in the process stream, which differ from application to application. To promote commercial deployment of these technologies, RD&D is needed to improve the performance of separation agents in the following areas:

- Selectivity required to achieve the desired separation
- Throughput (flux, loading capacity, etc.) required for reasonable system economics

- Sufficient durability to maintain optimum performance under the harsh industrial environments (i.e., severe pressures, temperatures, corrosiveness, fouling)
- Sufficient economies-of-scale incentive to be considered an alternative to established technologies in large-volume industrial processes

During a multi-stakeholder workshop sponsored by the National Science Foundation (NSF),[69] industry representatives identified the following three favorable conditions for adoption of PI technologies:[70]

- Applications where traditional economies of scale do not apply (e.g., remote locations, distributed supply chains)
- Applications where traditional technologies do not work (e.g., reactive separations for chemistries that require separation of intermediates for the reaction to proceed)
- Applications involving new construction or expansion versus retrofitting

High potential application areas identified by the industry group at the NSF-sponsored workshop include the following:[73]

- Chemical industries as an approach to improving reaction and separation efficiencies and increasing plant capacities
- Biorefining, being dominated by new construction and with distributed supply chains, making it amenable to adoption of PI technologies for smaller-scale, distributed production
- Stranded natural gas separations and conversion enabled by mobile, modular technologies
- Water management in remote locations and distributed manufacturing sites
- Carbon management for power generation to replace traditional technologies that do not scale well with low-pressure drops

Insights on RD&D strategies can be gleaned from the 2007 European PI roadmap.[71] First, the roadmap recognizes that, while overall cost competitiveness is a major focus for innovation of PI technologies, the benefits sought from PI implementations vary from chemical to chemical. For large volume production of petrochemicals and bulk chemicals, reducing energy costs and environmental impact are significant drivers of technology innovation. Conversely, energy costs make up a smaller fraction of the production costs for specialty chemicals and pharmaceuticals. In these industries, achieving improvements in selectivity, yield, and processing time is more important to their cost competitiveness.

The European roadmap identified 12 PI technologies with the greatest potential for the chemical industry and in need of fundamental and strategic research, namely, foam, monolith, micro, membrane, spinning disk, and heat exchanger reactors; membrane absorption/stripping; membrane adsorption; reactive extraction and extrusion; rotating packed beds; and rotor-stator mixers. For PI technologies that have been implemented in limited numbers of applications, support for applied research is needed, particularly making available pilot and prototype scale facilities for developing data and skills in the design of industrial-scale PI equipment.

Enabling technologies for successful industrialization of PI technologies noted in the European roadmap are as follows:

- In-situ measurement and analysis methods to better understand molecular level kinetic and thermodynamic characteristics of chemical processes
- Faster, more robust, nonlinear numerical modeling of chemical processes
- Process control systems of modular equipment

Process integration introduces unique process control challenges.[72] In these multifunctional systems, fewer degrees of freedom are available for control than there would be with divided single-purpose process steps. The desirable operating ranges for multifunctional systems are often narrower, yet owing to smaller spatial and temporal scales, the dynamics are more extreme. The development of customized on-line control algorithms based on fast and reliable process models are needed to address these challenges.

Risk, Uncertainty, and Other Considerations

Although PI technologies have been commercialized in the chemical industry, their application to different process chemistries are not without technical and financial risk. Significant RD&D investment, testing at bench through demonstration scale, and PI knowledge are required to develop, demonstrate, and design a first industrial application. For large-volume chemical production, whose processes have been incrementally optimized over time, the risks and RD&D investment needed to commercialize PI technologies may outweigh the potential energy and environmental benefits. In some cases, a viable solution to this barrier will be a paradigm shift away from billion-dollar, large-scale projects to strategically located, smaller, and less complex plants made possible by PI.

In addition, challenges need to be overcome in the large-scale manufacture of PI technologies. These challenges span materials processing (e.g., for defect-free membranes), fabrication of metal microstructures (e.g., for microchannel reactors), and incorporating materials with diverse properties into a single unit (e.g., for membrane reactors).[73] Innovative manufacturing solutions are needed to meet these challenges. Synergistic areas of DOE-sponsored RD&D include additive manufacturing, roll-to-roll processing, and advanced materials manufacturing.[74]

Cost reductions required to spur manufacturing and adoption of novel separation and PI technologies are likely to require sustained R&D investment and substantial commercial deployment. For several of the applications described in this technical assessment, government action may be needed to promote RD&D and commercial adoption. Regarding PI technologies, investment in demonstration and deployment will be important to transform the industrial economy-of-scale paradigm from scale-up (upsizing equipment) to “scale-out” (increasing modules).

In conclusion, the deployment of PI technologies could significantly reduce costs and energy use in high-value U.S. industries, including chemicals, biofuels, petroleum refining, mining, and oil and gas extraction. Additionally, PI approaches could lead to innovative solutions for addressing environmental challenges, including treatment of produced and waste waters as well as carbon capture.

Endnotes

[1] Van Gerven, Tom; Stankiewicz, Andrzej. "Structure, Energy, Synergy, Time—The Fundamentals of Process Intensification." Industrial & Engineering Chemistry Research, (48:5), 2009; pp. 2465-2474.

[2] Stankiewicz, A. I.; Moulijn, J. A. "Process Intensification: Transforming Chemical Engineering." Chemical Engineering Progress (96:1), 2000; pp. 22-34. (The authors categorize PI into "process intensifying equipment" and "process intensifying methods." The figure in this document adopts some of the categorization and examples from their "Figure 2. Process intensification and its components.")

[3] Tsouris, C.; Porcelli, J. V. "Process Intensification—Has Its Time Finally Come?" Chemical Engineering Progress October Issue 2003; pp. 50-55.

[4] Harmsen, Jan. "Process Intensification in the Petrochemicals Industry: Drivers and Hurdles for Commercial Implementation." Chemical Engineering and Processing: Process Intensification (49:1), 2010; pp. 70-73.

[5] Harmsen, G. J. "Reactive Distillation: The Front-runner of Industrial Process Intensification: A Full Review of Commercial Applications, Research, Scale-up, Design and Operation." Chemical Engineering and Processing: Process Intensification (46:9), 2007; pp. 774-780.

[6] Wood, David A.; Nwaoha, Chikezie; Towler, Brian F. "Gas-to-Liquids (GTL): A Review of an Industry Offering Several Routes for Monetizing Natural Gas." Journal of Natural Gas Science and Engineering (9), 2012; pp. 196-208.

[7] Drewes, J. E. An Integrated Framework for Treatment and Management of Produced Water—Technical Assessment of Produced Water Treatment Technologies. 1st edition. Golden, CO: Colorado School of Mines, 2009. RPSEA Project 07122-12.

[8] Environmental Protection Agency (EPA). Emerging Technologies for Wastewater Treatment and In-Plant Wet Weather Management. EPA 832-R-12-011, March 2013.

[9] Spoorthi, G.; Thakur, R. S.; Kaistha, N.; Rao, D. P. "Process Intensification in PSA Processes for Upgrading Synthetic Landfill and Lean Natural Gases." Adsorption, 17(1), 2011; pp. 121-133.

[10] Anderson, M. A.; Cudero, A. L.; Palma, J. "Capacitive Deionization as an Electrochemical Means of Saving Energy and Delivering Clean Water. Comparison to Present Desalination Practices: Will It Compete?" Electrochimica Acta, 55(12), 2010; pp. 3845-3856.

[11] Szymcek, P.; McCallum, S. D.; Taboada-Serrano, P.; Tsouris, C. "A Pilot-scale Continuous-Jet Hydrate Reactor." Chemical Engineering Journal, 135(1), 2008; pp. 71-77.

[12] "Shale Gas: Reshaping the US Chemicals Industry." PricewaterhouseCoopers LLW, 2012: http://www.pwc.com/en_US/us/industrial-products/publications/assets/pwc-shale-gas-chemicals-industry-potential.pdf.

[13] Manufacturing Energy and Carbon Footprints (2010 MECS), U.S. Department of Energy Office of Energy Efficiency & Renewable Energy. Available from: http://energy.gov/eere/amo/manufacturing-energy-and-carbon-footprints-2010-mecs.

[14] Creative Energy. "European Roadmap for Process Intensification." 2007.

[15] Top Value Added Chemicals from Biomass; Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas. Pacific Northwest National Laboratory, National Renewable Energy Laboratory, BETO, 2004. Available from: http://www1.eere.energy.gov/bioenergy/pdfs/35523.pdf.

[16] Top Value Added Chemicals from Biomass; Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas. Pacific Northwest National Laboratory, National Renewable Energy Laboratory, BETO, 2004.

[17] "End Use—DOE Energy Information Agency's Annual Energy Outlook 2013 Reference Case." "Feedstocks—DOE Energy Information Agency's Manufacturing Energy Consumption Survey (MECS)," Table 2.2 (where data was given). Both are publically available from: http://www.eia.gov/.

[18] "Annual Energy Outlook 2014." Department of Energy, Energy Information Agency, 2014.

[19] American Chemical Council, News Release, http://www.americanchemistry.com/Media/PressReleasesTranscripts/ACC-news-releases/Economic-Outlook-for-US-Chemical-Industry-Strong.html See also: American Chemistry Council. "Year-End 2013 Chemical Industry Situation and Outlook." Washington, DC, 2013

[20] ACC (September 2015) U.S. Chemical Investment Linked to Shale Gas:$153 billion and Counting. http://www.americanchemistry.com/Policy/Energy/Shale-Gas/Fact-Sheet-US-Chemical-Investment-Linked-to-Shale-Gas.pdf

[21] Manufacturing Energy Consumption Survey (MECS) 2010, Table 2.2 footnote: For the petroleum refining industry only, the yellow bar includes only those feedstocks that are used to produce nonenergy products (i.e., asphalt, waxes, lubricants, and solvents) and feedstocks for adjoining petrochemical plants. Feedstocks that were converted in the petroleum refining industry to other energy products (e.g., crude oil converted to residual and distillate fuel oils) are excluded. Available from: http://www.eia.gov/consumption/manufacturing/data/2010/pdf/Table2_2.pdf.

[22] Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S Chemical Manufacturing prepared by Energetics, Inc. for the U.S. DOE Advanced Manufacturing Office, 2015, available from: http://www.energy.gov/eere/amo/downloads/bandwidth-study-us-chemical-manufacturing

[23] LPG includes propane, propylene, n- and iso-butane, and butylene.

[24] Creative Energy. "European Roadmap for Process Intensification," 2007. Available from: http://www.efce.info/efce_media/-p-531.pdf?rewrite_engine=id.

[25] Chemical Bandwidth Study. Prepared by JVP International and Energetics, Inc., for U.S. DOE, Industrial Technologies Program, 2006 (draft). Available from: http://www.energy.gov/eere/amo/downloads/itp-chemicals-chemical-bandwidth-study-energy-analysis-powerful-tool-identifying

[26] Energetics (study in progress).

[27] Tonkovich, A. Y.; Zilka, J. L.; LaMont, M. J.; Wang, Y.; Wegeng, R. S. "Microchannel Reactors for Fuel Processing Applications. I. Water Gas Shift Reactor." Chemical Engineering Science, 54(13), 1999; pp. 2947-2951.

[28] DOE Factsheet. (2011) "Process Intensification with Integrated Water-Gas-Shift Membrane Reactor." Available from: http://energy.gov/sites/prod/files/2013/11/f4/water-gas-shift.pdf.

[29] Delfrate, A.; Schmitt, C., Stolten, D., Grube, T. "Integration of Fuel Cells Systems into Chlor Alkali Plants: The Chlorine Industry Perspective." 18th World Hydrogen Energy Conference; Essen (Germany), 2010.

[30] Bernardo, P.; Drioli, E.; Golemme, G. "Membrane Gas Separation: A Review/State of the Art." Industrial & Engineering Chemistry Research, 48(10), 2009; pp. 4638-4663.

[31] Dyer, P. N.; Richards, R. E.; Russek, S. L.; Taylor, D. M. "Ion Transport Membrane Technology for Oxygen Separation and Syngas Production." Solid State Ionics, 134(1), 2000; pp. 21-33.

[32] Iwakabe, Koichi; Nakaiwa, Masaru; Huang, Kejin; Nakanishi, Toshinari; Røsjorde, Audun; Ohmori, Takao; Endo, Akira; Yamamoto, Takuji. "Energy Saving in Multicomponent Separation Using an Internally Heat-Integrated Distillation Column (HIDiC)." Applied Thermal Engineering (26:13), 2006; pp. 1362-1368.

[33] A portion of the 563 TBtu/year results from the potential energy savings of the implementation of best practices and state-of-the-art commercial equipment.

[34] Based on a simplified value of $13.091/MMBtu (calculated average of the industrial price of electricity and natural gas). Energy Information Agency (EIA), 2014: http://www.eia.gov/electricity/annual/html/epa_01_01.html and http://www.eia.gov/dnav/ng/hist/n3035us3m.html. Note: In the bulk chemical sector, the EIA Annual Energy Outlook 2014 Reference Case weighted average electricity and feedstock natural gas for ranges between $12.52/MMBtu and $16.89/MMBtu across the forecast, 2012 to 2040: http://www.eia.gov/forecasts/aeo/tables_ref.cfm.

[35] International Energy Agency, International Council of Chemical Associations & DeChema. "Technology Roadmap: Energy and GHG Reductions in the Chemical Industry via Catalytic Processes." 2013. Available from: http://www.iea.org/publications/freepublications/publication/Chemical_Roadmap_2013_Final_WEB.pdf.

[36] Fallas, B.; Pavlov, P. Platts. Special Report: Petrochemicals, Time to Get Cracking. New York: McGraw-Hill Companies, Inc., 2013.

[37] Bernardo, P.; Barbieri, G.; Drioli, E. "An Exergetic Analysis of Membrane Unit Operations Integrated in the Ethylene Production Cycle." Chemical Engineering Research and Design, 84(5), 2006; pp. 405-411.

[38] Jiang, H.; Cao, Z.; Schirrmeister, S.; Schiestel, T.; Caro, J. "A Coupling Strategy to Produce Hydrogen and Ethylene in a Membrane Reactor." Angewandte Chemie International Edition, 49(33), 2010; pp. 5656-5660.

[39] Freemantle, M.; London, C. "Pilot Plant Velocys' Facility in Plain City, Ohio, Has Several Automated Enclosures for Testing Microchannel Devices. Velocys Photo." Science & Technology, 82(41), 2004; pp. 39-43.

[40] Yang, B.; Yuschak, T.; Mazanec, T.; Tonkovich, A. L.; Perry, S. "Multi-scale Modeling of Microstructured Reactors for the Oxidative Dehydrogenation of Ethane to Ethylene." Chemical Engineering Journal, 135, 2008; pp. S147-S152.

[41] Chen, G.; Li, S.; Jiao, F.; Yuan, Q. "Catalytic Dehydration of Bioethanol to Ethylene over TiO2/γ-Al2O3 Catalysts in Microchannel Reactors." Catalysis Today, 125(1), 2007; pp. 111-119.

[42] Safarik, D. J.; Eldridge, R. B. "Olefin/Paraffin Separations by Reactive Absorption: A Review. Industrial & Engineering Chemistry Research, 37(7), 1998; pp. 2571-2581.

[43] Chen, J.; Eldridge, R. B.; Rosen, E. L.; Bielawski, C. W. "A Study of Cu(I)-Ethylene Complexation for Olefin–Paraffin Separation." AIChE Journal, 57(3), 2011; pp. 630-644.

[44] Zhang, Yiming; Li, Baiyan; Krishna, Rajamani; Wu, Zili; Ma, Dingxuan; Shi, Zhan; Pham, Tony; Forrest, Katherine; Space, Brian; Ma, Shengqian. "Highly Selective Adsorption of Ethylene over Ethane in a MOF Featuring the Combination of Open Metal Site and π-Complexation." Chemical Communications, 2015.

[45] Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. "Hydrocarbon Separations in a Metal-Organic Framework with Open Iron. II. Coordination Sites." Science, 335(6076), 2012; pp. 1606-1610.

[46] Technologies and metrics are from Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S Chemical Manufacturing, prepared by Energetics, Inc., for the U.S. DOE Advanced Manufacturing Office (to be published 2015).

[47] Refer to pg 381 of Chapter 10 of the 2015 Quadrennial Technology Review for a more detailed description of Technology Readiness Levels (http://energy.gov/sites/prod/files/2015/09/f26/QTR2015-10-Integrated-Analysis.pdf). See also Banke, J. "Technology Readiness Levels Demystified." National Aeronautics and Space Administration (NASA), August 20, 2010. Accessed February 5, 2015: http://www.nasa.gov/topics/aeronautics/features/trl_demystified.html.

[48] Ng, S.; Fairbridge, C.; Mutyala, S.; Liu, Y.; Bélanger, J. R.; Paré, J. R. J. "Microwave-Assisted Conversion of Ethane to Ethylene," Applied Petrochemical Research, vol. 3, 2013; pp. 55-61.

[49] Fall, M.; Wagner, E.; Cabe, F.; Eagleson, G.; Carnahan, J.; Lal, R., et al., "Microwave Enhanced Cracking of Ethane for Ethylene Production," presented at the 24th Annual Ethylene Producers Conference, Houston, Texas, 2012.

[50] Energetics (study in progress).

[51] "What Is a Biorefinery?" National Renewable Energy Laboratory, 2009. Accessed February 3, 2015: http://www.nrel.gov/biomass/biorefinery.html.

[52] Sanders, J. P. M.; Clark, J. H.; Harmsen, G. J.; Heeres, H. J.; Heijnen, J. J.; Kersten, S. R. A.; Van Swaaij, W. P. M.; Moulijn, J. A. "Process Intensification in the Future Production of Base Chemicals from Biomass." Chemical Engineering and Processing: Process Intensification (51), 2012; pp. 117-136.

[53] He, Y.; Bagley, D. M.; Leung, K. T.; Liss, S. N.; Liao, B. Q. "Recent Advances in Membrane Technologies for Biorefining and Bioenergy Production." Biotechnology Advances, 30(4), 2012; pp. 817-858.

[54] Datta, S.; Lin, Y. P. J.; Snyder, S. W. "Current and Emerging Separation Technologies Used in Biorefining", in Advances in Biorefineries, Waldron, K., ed., Woodhead Publishing Series in Energy, Cambridge, UK, 2014; pp. 112-151. DOI: 10.1533/9780857097385.1.112.

[55] Datta, S.; Henry, M.P.; Lin, Y. J.; Fracaro, A. T,; Millard, C. S.; Snyder, S. W.; Stiles, R. L.; Shah, J.; Yuan, J.; Wesoloski, L.; Dorner, R. W.; Carlson, W. M. "Electrochemical CO2 Capture Using Resin-Wafer Electrodeionization (RW-EDI)," Industrial and Engineering Chemistry Research, 52(43), 2013; pp. 15177-15186.

[56] Yupo J. Lin, Jamie A. Hestekin, Michael P. Henry, Norman Sather, Chapter 9: Bioprocessing of Cost-Competitive Biobased Organic Acids, , in: Snyder S.W., editor, Commercializing Biobased Products: Opportunities, Challenges, Benefits, and Risks. Royal Society of Chemistry, Cambridge, UK, 2015

[57] Huang, H. J.; Ramaswamy, S.; Tschirner, U. W.; Ramarao, B. V. "A Review of Separation Technologies in Current and Future Biorefineries." Separation and Purification Technology, 62(1), 2008; pp. 1-21.

[58] Frolkova, A. K.; V. M. Raeva. "Bioethanol Dehydration: State of the Art." Theoretical Foundations of Chemical Engineering, (44:4) 2010; pp. 545-556.

[59] Kiss, Anton A.; Suszwalak, David J. "Enhanced Bioethanol Dehydration by Extractive and Azeotropic Distillation in Dividing-Wall Columns." Separation and Purification Technology (86), 2012; pp. 70-78.

[60] Qiu, Zheyan; Zhao, Lina; Weatherley, Laurence. "Process Intensification Technologies in Continuous Biodiesel Production." Chemical Engineering and Processing: Process Intensification (49:4), 2010; pp. 323-330.

[61] Oak Ridge National Laboratory Factsheet, "Manufacturing Biodiesel from Triglycerides," UT-B IDs 200702012, 200701972, 200802186, 2011.

[62] BCS, Incorporated, and Oak Ridge National Laboratory. Materials for Separation Technologies: Energy and Emission Reduction Opportunities. Report prepared for the U.S. DOE, Industrial Technologies Program, 2005.

[63] BCS, Incorporated; ORNL. "Materials for Separation Technologies: Energy and Emission Reduction Opportunities." May 4, 2005.

[64] Drioli, E.; Stankiewicz, A. I.; Macedonio, F. "Membrane Engineering in Process Intensification—An Overview." Journal of Membrane Science, 380(1), 2011; pp. 1-8.

[65] Adapted from BCS, Incorporated, and Oak Ridge National Laboratory. Materials for Separation Technologies: Energy and Emission Reduction Opportunities. May 4, 2005. http://sst.ornl.gov/Guidelines/abstract_example.pdf

[66] QTR, Chapter 6, Technology Assessment 6.B "Advanced Materials Manufacturing" http://www.energy.gov/qtr.

[67] Cybulski, A.; Moulijn, J. A.; Stankiewicz, A. (eds.). Novel Concepts in Catalysis and Chemical Reactors: Improving the Efficiency for the Future. John Wiley & Sons, 2011.

[68] QTR, Chapter 6, Technology Assessment 6.B "Advanced Sensors, Control, Platforms, and Modeling for Manufacturing" http://www.energy.gov/qtr

[69] National Science Foundation. 2014. Process Intensification Workshop. Available from: http://www.aiche.org/sites/default/files/docs/conferences/pi_workshop_report_11-10_a-2-final.pdf.

[70] Robinson, S. Private communication: Notes from the National Science Foundation-Sponsored Process Intensification Workshop, September 30–October 1, 2014, Virginia Tech Executive Briefing Center, 2014.

[71] Creative Energy. "European Roadmap for Process Intensification." 2007. Available from: http://www.efce.info/efce_media/-p-531-EGOTEC-34kdll9fiqnru8376q05juj2d2.pdf?rewrite_engine=id

[72] Nikačević, N. M.; Huesman, A. E.; Van den Hof, P. M.; Stankiewicz, A. I. "Opportunities and Challenges for Process Control in Process Intensification." Chemical Engineering and Processing: Process Intensification (52), 2012; pp. 1-15.

[73] National Science Foundation. 2014. Process Intensification Workshop. Available from: http://www.aiche.org/sites/default/files/docs/conferences/pi_workshop_report_11-10_a-2-final.pdf.

[74] Reference the "Additive Manufacturing," "Roll-to-Roll," and "Advanced Materials Manufacturing" technology assessments.

Acronyms

DWC	Divided wall column
PI	Process intensification
FT	Fischer-Tropsch
Bpd	Barrels per day
MSCFD	Million standard cubic feet per day
NGLs	Natural gas liquids
LPGs	Liquefied petroleum gases
CT	Current typical
PM	Practical minimum
MOF	Metal organic frameworks
COP	Cost of production
EDI	Electrodeionization
ED	Electrodialysis
IX	Ion exchange
MMBtu	Million british thermal units
TBtu	Trillion british thermal units
TRL	Technology readiness level

Glossary

Monolith reactor
A reactor whose catalyst is supported by a single block structure, whose design enhances mass and heat transfer (moulijn, jacob a., And freek kapteijn. "Monolithic reactors in catalysis: excellent control." Current opinion in chemical engineering 2, no. 3 (2013): 346-353.)

Foam reactor
A type of monolith reactor with a solid foam catalytic support, whose open pore structure provides high surface area, small diffusion lengths, and low pressure drop (moulijn & kapteijn 2013)

Microreactors
Also known as micro-channel reactors: a continuous flow reactor where reagents are passed through and reaction in narrow (10-1000 Qm) channels. (Mason, b. P., Price, k. E., Steinbacher, j. L., Bogdan, a. R., & Mcquade, d. T. (2007). Greener approaches to organic synthesis using microreactor technology. Chemical reviews, 107(6), 2300-2318.)

Membrane reactor
A reactor equipped with a membrane that can serve either as an extractor to remove products to shift equilibrium, as a distributor to control the addition of reactants, or as an active contactor to control diffusion of reactants (ravanchi, m. T., Kaghazchi, t., & Kargari, a. (2009). Application of membrane separation processes in petrochemical industry: a review. Desalination, 235(1), 199-244.)

Spinning disk reactor
A reactor equipped with a horizontally oriented plate that rotates at speeds up to 5000 rpm on which a thin film or reagents react under conditions of short residence time and high heat and mass transfer (van gerven, tom, guido mul, jacob moulijn, and andrzej stankiewicz. "A review of intensification of photocatalytic processes." Chemical engineering and processing: process intensification 46, no. 9 (2007): 781-789.)

Heat exchanger reactors
(Also known as compact heat exchanger reactors or hex reactors): a reactor that is a heat exchanger in which reactions occur, where the heat exchanger may take different forms including plate-type, metal foam, and microstructure (anxionnaz, zoé, michel cabassud, christophe gourdon, and patrice tochon. "Heat exchanger/reactors (hex reactors): concepts, technologies: state-of-the-art." Chemical engineering and processing: process intensification 47, no. 12 (2008): 2029-2050.)

Electrodialysis
A technology applies an electric current to transport ions through an ion-exchange membrane to affect species separations (xu, t., & Huang, c. (2008). Electrodialysis-based separation technologies: a critical review. Aiche journal, 54(12), 3147-3159.)

Reactive extraction
A liquid-liquid extraction process that deploys a specified extractant that reacts with the solute to increase the distribution coefficient for recovering it (bart, dipl-ing dr hans-jörg. Reactive extraction. Springer berlin heidelberg, 2001.)

Rotating packed beds	Equipment, which is designed for countercurrent gas/liquid separations, that is equipped with an annular, cylindrical packed bed rotated at speeds of 500-2000 rpm to create centrifugal force for improved separation efficiency (rao, d. P., A. Bhowal, and p. S. Goswami. "Process intensification in rotating packed beds (higee): an appraisal." Industrial & engineering chemistry research 43, no. 4 (2004): 1150-1162.)
Rotor-stator mixers	A high shear mixer that has a rotating bladed or teethed part, which spins at high speeds (10-50 meters/second), that is narrowly spaced within a complementarily designed static part (zhang, jinli, shuangqing xu, and wei li. "High shear mixers: a review of typical applications and studies on power draw, flow pattern, energy dissipation and transfer properties." Chemical engineering and processing: process intensification 57 (2012): 25-41.)