

Process Intensification – Chemical Sector Focus Technology Assessment

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1. Introduction

Process Intensification (PI) targets dramatic improvements in manufacturing and processing by rethinking existing operation schemes into ones that are both more precise and efficient than existing operations. 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 economical manufacturing process. At the molecular level, PI technologies significantly enhance mixing, which improves mass and heat transfer, reaction kinetics, yields, and specificity. 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 (2009) provide four guiding principles for PI¹:

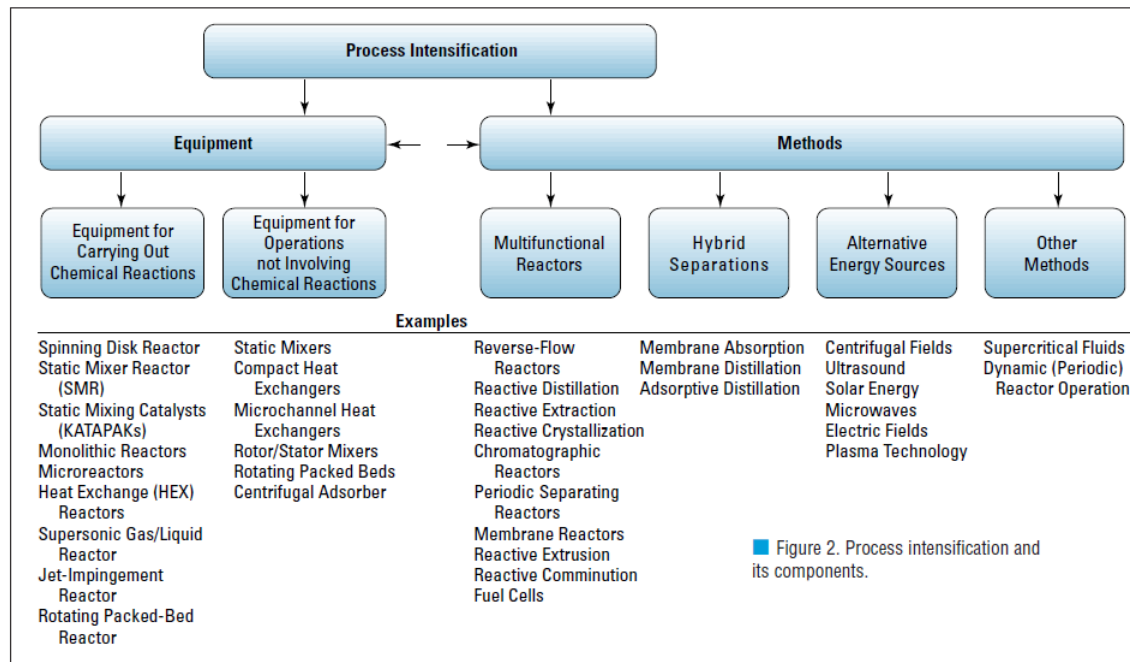
- Maximize effectiveness of intramolecular and intermolecular events (example: dynamically changing conditions to attain kinetic regimes with higher conversion and selectivity)
- Provide all molecules the same process experience (example: plug flow reactor with uniform, gradient-less heating)
- Optimize 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)

¹ Van Gerven, Tom, and Andrzej Stankiewicz. "Structure, energy, synergy, time -- The fundamentals of process intensification." *Industrial & engineering chemistry research* 48, no. 5 (2009): 2465-2474.

37
 38 PI designs that achieve all or some of these molecular-level optimal conditions are likely to be
 39 transformative. Reactors that enable precise control of the reactor environment could dramatically
 40 increase yields, conversions, and selectivity, which in turn would reduce material, energy, and
 41 carbon intensities, minimize purification needs, and reduce waste disposal burdens. Additionally,
 42 PI technologies could enable the manufacture of products that otherwise could not be safely or
 43 successfully made.

44
 45 Figure 1 displays a taxonomy of PI technologies as formulated by Stankiewicz and Moulijn (2000)².
 46 PI equipment is characterized by designs that optimize mass, heat, and momentum transfer (e.g.,
 47 microreactors, spinning disk reactors, static mixers, monolithic catalysts). PI methods involve
 48 integration of multiple processing steps (e.g., reactive distillation, membrane reactors, hybrid
 49 separations, multicomponent distillation, fuel cells) and application of alternative energy sources
 50 (e.g., microwaves, magnetic forces, ultrasound, centrifugal fields).

51
 52



■ Figure 2. Process intensification and its components.

53
 54 *Figure 1 Taxonomy of PI technologies*

55 **Need to redraw – cite Stankiewicz and Moulijn (2000)**

56
 57
 58 Commercial applications of PI date back to the 1970s. Static mixers, which are ubiquitous today,
 59 were early PI inventions. Other early PI technologies deployed reactive distillation, including
 60 Eastman Chemical Company’s tower reactor, which integrated five processing steps in the
 61 production of methyl acetate from methanol, achieving an 80% reduction in energy and a large

² Stankiewicz, A. I., & Moulijn, J. A. (2000). Process intensification: transforming chemical engineering. *Chemical Engineering Progress*, 96(1), 22-34.

62 reduction in capital cost³. In the chemical industry, reactive distillation, divided wall column
 63 distillation, and reverse flow reactors have been commercialized each with more than 100
 64 installations as shown in Table 1⁴. Drivers for PI innovation include the potential for reduction in
 65 feedstock cost, capital expenditure, energy, and safety issues. Barriers to deployment include risk
 66 of failure, scale-up unknowns, unreliability of equipment, and uncertain safety, health, and
 67 environmental impacts.

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Table 1 Commercial application of PI technologies in the petrochemical industry

J. Harmsen / Chemical Engineering and Processing 49 (2010) 70–73

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Table 1
 Process intensification technologies in the petrochemical industry and their innovation drivers.

Technologies	Innovation drivers				Commercial implementation
	Feedstock cost reduction	Capital cost reduction	Energy reduction	Inherently safe	
Reactive distillation		20–80%	20–80%	+	>150
DWC distillation		10–30%	10–30%		>100
Reverse flow reactor		>20%	Low		>100
Microchannels reactor	Yes	Yes for small scale		+	Only in fine chemicals sector
High gravity absorbers	Yes; case dependent	Yes; case dependent			A few
External field PI					

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 72
 73
 74
 75

Reconstruct this table to include the first 3 technologies only with capital cost reduction, energy reduction, and commercial implementation, cite Harmsen 2010

76 Applications for PI technologies crosscut energy-intensive industries with opportunity space in
 77 chemicals, petroleum refining, plastics, forest products, oil and gas production, and food industries
 78 among others. PI innovation could deliver solutions to energy security, environmental, and
 79 economic challenges in areas ranging from stranded gas recovery, carbon capture, and water
 80 treatment. Commercial endeavors in these areas include microchannel reactors for converting
 81 natural gas to fuels at the well site (see text box)⁵. vibratory shear enhanced membrane filtration
 82 for produced water treatment⁶, and reactive media filtration for nutrient removal in waste waters⁷.
 83 PI technologies under development include novel pressure swing adsorption for upgrading lean
 84 natural gases⁸, capacitive deionization for water desalination⁹, and continuous jet hydrate reactors

³ Tsouris, C., and J.V. Porcelli. Process Intensification – Has Its Time Finally Come? *Chemical Engineering Progress* October 2003

⁴ Harmsen, Jan. "Process intensification in the petrochemicals industry: drivers and hurdles for commercial implementation." *Chemical Engineering and Processing: Process Intensification* 49, no. 1 (2010): 70-73.

⁵ Wood, David A., Chikezie Nwaoha, and Brian F. Towler. "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): 196-208.

⁶ Drewes, J. E. (2009). 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. RPSEA Project 07122-12

⁷ EPA (2013). Emerging Technologies for Wastewater Treatment and In-Plant Wet Weather Management. EPA 832-R-12-011. March 2013.

⁸ Spoorthi, G., Thakur, R. S., Kaistha, N., & Rao, D. P. (2011). Process intensification in PSA processes for upgrading synthetic landfill and lean natural gases. *Adsorption*, 17(1), 121-133.

⁹ Anderson, M. A., Cudero, A. L., & Palma, J. (2010). 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), 3845-3856

85 for continuous injection of CO₂ hydrate in the deep ocean¹⁰. In these application areas, where
86 environmental regulations are 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. AMO supported the microchannel reactor research that successfully developed 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. Typical design throughputs are 15-150 MSCFD natural gas, producing 1,500 to 10,000 barrels of liquid product. Velocys has entered a joint venture with Waste Management, NRG Energy, and Ventech Engineers, for a commercial plant under construction in Oklahoma City, OK, and expected to startup in 2016.

Challenges in the 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.

87
88 This technical assessment focuses on applications in the chemical industry, where PI is a key
89 development platform for efficient chemicals production. Technology evolution in the chemical
90 industry needs to emphasize more efficient processes for the purpose of safely reducing production
91 cost and energy consumption. In addition, the United States is uniquely positioned to benefit from
92 the increased access to shale gas by hydraulic fracturing, or fracking. Feedstock diversity (either
93 through an increased used of domestic natural gas or biomass) is expected to enhance the U.S.
94 chemical sector's competitiveness and environmental footprint. To that point,
95 PricewaterhouseCoopers LLW (PwC)¹¹ predicts higher profit margins and global exports for
96 chemicals from shale gas, particularly ethylene. PwC estimates that the cost of producing ethylene
97 from ethane in the U.S. fell from just under \$1000 per ton to just over \$300 per ton, accredited to
98 the drop in energy and feedstock prices experienced over the period 2008 to 2012.
99
100 The chemicals sector is the most energy-intensive of all industrial sectors, with primary energy use
101 of approximately 4.3 Quad and combustion emissions of about 252 million tonnes of carbon dioxide
102 equivalents in 2010¹². A European roadmapping analysis¹³ concluded that R&D investment in PI
103 technologies could lead to improvement in overall energy efficiency of petrochemical and bulk
104 chemical production by 20% in 30-40 years and to a 50% reduction in costs for specialty chemicals
105 and pharmaceuticals production in 10-15 years.

¹⁰ Szymcek, P., McCallum, S. D., Taboada-Serrano, P., & Tsouris, C. (2008). A pilot-scale continuous-jet hydrate reactor. *Chemical Engineering Journal*, 135(1), 71-77.

¹¹ PwC (2012). "Shale gas: Reshaping the US chemicals industry."
http://www.pwc.com/en_US/us/industrial-products/publications/assets/pwc-shale-gas-chemicals-industry-potential.pdf

¹² Brueske, S., C. Kramer, and A. Fisher (2014). U.S. Chemical Industry Energy Use Bandwidth Study. (Draft)

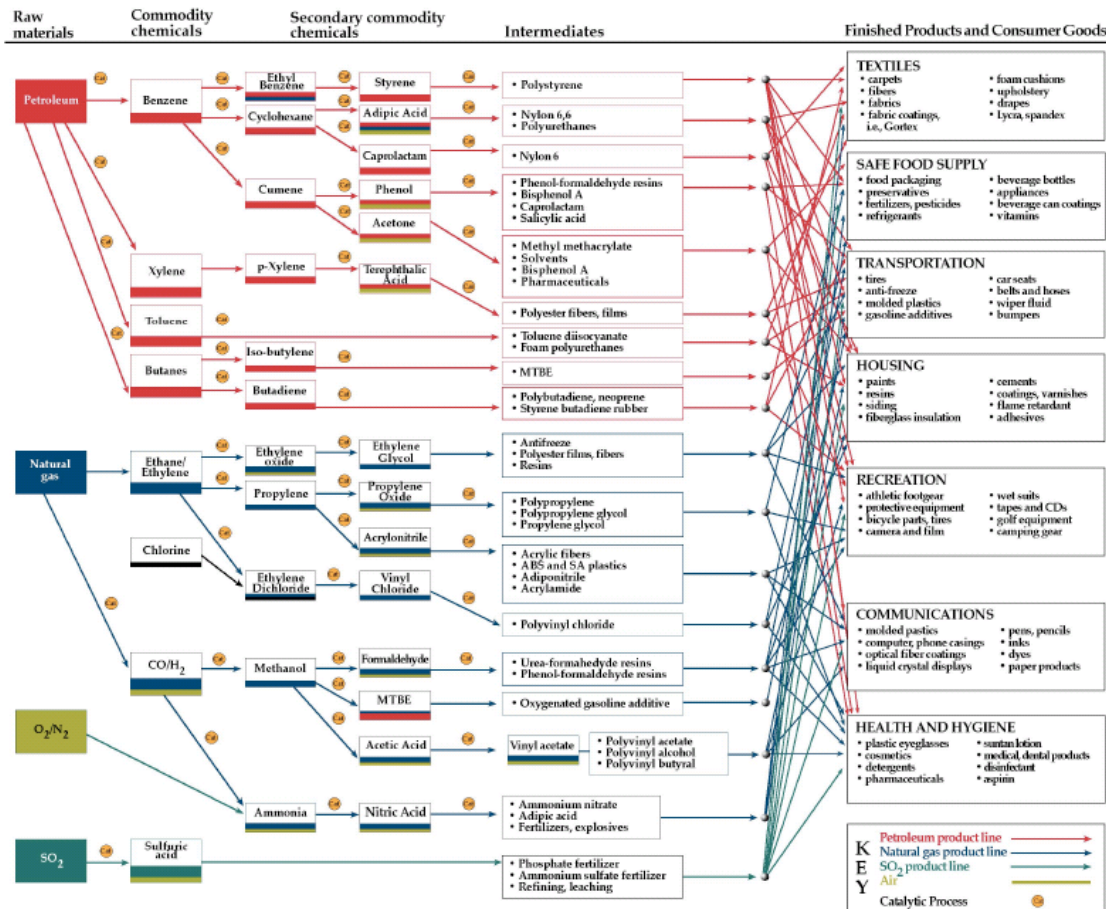
¹³ Creative Energy (2007). "European Roadmap for Process Intensification"

106 **2. Technology Assessment and Potential**

107 **2.1 Chemical Industry Focus**

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110 In the U.S., nearly 14 thousand manufacturers in the chemicals industry transform raw materials
111 into more than 70,000 compounds, which are used to produce nearly every product in use today,
112 including plastics, paper, paints, cleaners, adhesives, pharmaceuticals, cosmetics, textiles, building
113 materials, food packaging, appliances, and electronic devices. As shown in Figure 2, the production
114 of commodity chemicals from raw materials are converted to intermediates which span multiple
115 sectors of the U.S. economy in areas of textiles, safe food supply, transportation, housing, recreation,
116 communications, and health and hygiene products and goods¹⁴.

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119 **Figure 2 Chemical manufacturing pathways¹⁵**

¹⁴ PNNL, NRE, BETO. (2004). *Top Value Added Chemicals from Biomass; Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas.*

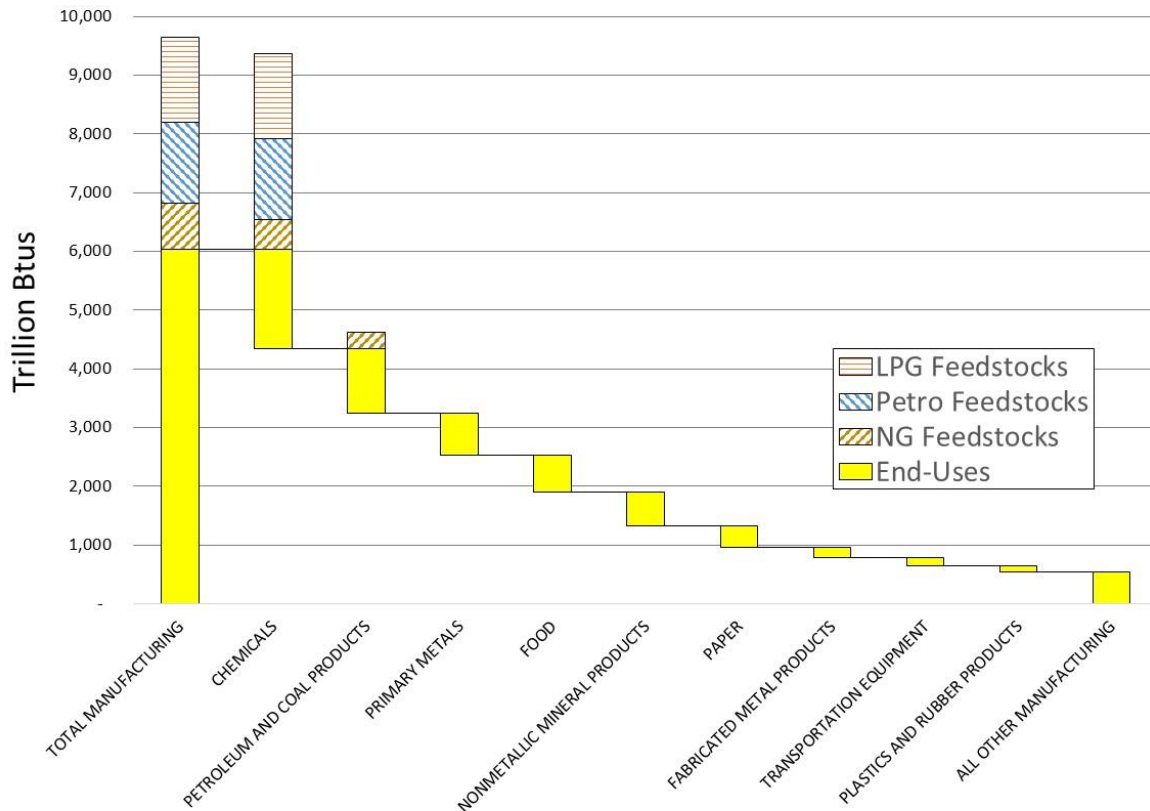
http://nrelpubs.nrel.gov/Webtop/ws/nich/www/public/Record?rpp=25&upp=0&m=2&w=NATIVE%28%27TITLE_V+ph+words+%27%27Top+Value+Added+Chemicals+from%27%27%29&order=native%28%27pubyear%2FDescend%27%29

¹⁵ PNNL, NRE, BETO. (2004). *Top Value Added Chemicals from Biomass; Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas.*

<http://nrelpubs.nrel.gov/Webtop/ws/nich/www/public/Record?rpp=25&upp=0&m=2&w=NATIVE%28%27>

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Data plotted in Figure 3 show the chemical industry to be the largest consumer of petroleum and natural gas based feedstock in the industrial sector. 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 (NGL)¹⁶. 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 3.5% growth in U.S. chemical output in 2015 and over 4% per year average to 2020¹⁷. By 2018, the ACC forecasts capital spending in the U.S. chemical industry to reach \$61 billion. The renewed investment health 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.



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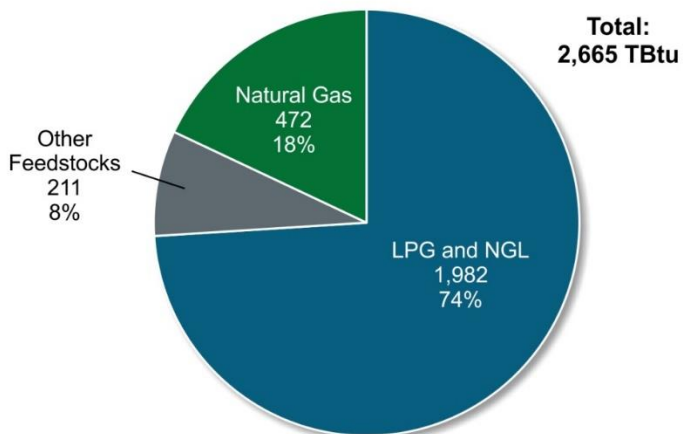
Figure 3 - Feedstock consumption by the Top 10 energy consuming manufacturing sectors

[7TITLE V+ph+words+%27%27Top+Value+Added+Chemicals+from%27%27%27%29&order=native%28%27pubyear%2FDescend%27%29](#)

¹⁶ DOE Energy Information Agency. (2014) Annual Energy Outlook 2014.

¹⁷ American Chemistry Council. (2013). Year-End 2013 Chemical Industry Situation and Outlook. Washington DC.

138 Figure 4 shows feedstock energy use in the U.S. chemical industry¹⁸. The chemicals sector
 139 consumed 2,665 TBtu of feedstock energy in 2010. Liquefied petroleum gases (LPG)¹⁹ and natural
 140 gas liquids (NGLs) account for 74% of the feedstock energy used, while natural gas provided 18%,
 141 and other feedstocks (including fuel oil, coal, coke and breeze, and other energy feeds) provided the
 142 remainder. Of the 2,665 TBtu of feedstock energy, 85% ends up in the form of finished chemical
 143 products. The remaining 15% (400 TBtu/yr) provides an opportunity window for PI solutions
 144 targeted at improving chemical reaction selectivity and process yield.



145
 146 *Figure 4 Feedstock energy consumption in the chemical sector, 2010*²⁰

147 2.2 PI Technologies for the Chemical Industry

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 149 Applications of PI technologies need to be evaluated in the context both of the PI equipment or
 150 method and the specific chemistry and processes used to produce the chemical. Evaluations of the
 151 former, as discussed in this section, need to be qualified as insufficient in determining their
 152 application for the production of a specific chemical. The latter must be considered chemical by
 153 chemical. In section 2.2, PI applications for select energy consuming chemicals are discussed, with
 154 a focus on chemicals produced from natural gas (methane) and NGL feedstock. PI applications for
 155 chemicals produced from biomass feedstock are discussed in section 2.3. PI technologies for
 156 separations are addressed in section 2.4.

157
 158 A 2007 European road mapping analysis²¹ assessed PI technologies according to their generic
 159 potential to save energy, improve cost competitiveness, and reduce CO₂ emissions, as well as their
 160 maturity and likelihood to overcome barriers to adoption. High, medium, and low judgments were
 161 made for each PI technology and each commercial value metric. The PI technologies which were
 162 deemed to have high or medium potential for energy savings are listed in Table 2. These valuations
 163 are the product of a team of experts and reflect their experience and judgment at a particular
 164 period of time.
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¹⁸ Brueske, S., C. Kramer, and A. Fisher (2014). U.S. Chemical Industry Energy Use Bandwidth Study. (Draft)

¹⁹ LPG includes propane, propylene, n- and iso-butane, butylene.

²⁰ Brueske, S., C. Kramer, and A. Fisher (2014). U.S. Chemical Industry Energy Use Bandwidth Study. (Draft)

²¹ Creative Energy (2007). "European Roadmap for Process Intensification"

167 *Table 2 PI technologies with high and medium potential for energy savings as assessed for European*
 168 *Roadmap*

PI Equipment or Method	Potential for energy savings	Potential to improve cost competitiveness	Potential to reduce CO2	Maturity of technology	Likelihood 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
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
Reactive extraction columns, HT and HS	medium	low	medium	medium	high
Extractive distillation	medium	low	low	medium	medium

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170 **PI Technologies for Energy Consuming Chemicals**

171

172 The 2006 *Chemical Bandwidth Study*²² and the 2014 *U.S. Chemical Industry Energy Bandwidth*
 173 *Study*²³ identified some of the top energy consuming chemicals in the United States. Based on the
 174 Bandwidth analysis, 11 chemicals (listed in descending order of energy consumption) have been
 175 identified to have significant opportunity for energy savings via the implementation of PI
 176 technologies.

- | | | |
|----------------------------------|----------------------|-------------------|
| 1. Ethylene | 5. Nitrogen/Oxygen | 9. Ethylene Oxide |
| 2. Ethanol | 6. Propylene | 10. Methanol |
| 3. Chlorine/
Sodium Hydroxide | 7. Terephthalic Acid | 11. Hydrogen |
| 4. Ammonia | 8. Carbon Black | |

²² *Chemical Bandwidth Study*. Draft. Prepared by JVP International and Energetics, Inc. for U.S. Department of Energy, Industrial Technologies Program. 2006. http://energy.gov/sites/prod/files/2013/11/f4/chemical_bandwidth_report.pdf

²³ *Chemical Industry Energy Bandwidth Study*. Prepared by Energetics, Inc. for U.S. Department of Energy, AMO. 2014.

177
 178 In 2010, the production processes for these chemicals utilized 1,152 TBtu/yr, accounting for 63%
 179 of the total onsite energy consumed in the chemicals industry as shown in Table 3. Also in this
 180 table are shown estimates of the energy reduction opportunity from successful development and
 181 implementation of PI technologies for each of the chemicals, totaling 563 TBtu/yr²⁴. Using a
 182 simplified assumption of \$13.09/ MMBtu²⁵ for industrial energy, these savings equate to a potential
 183 annual cost of production (COP) savings of \$7.4 billion.

184
 185 *Table 3 2010 Production, energy consumption, cost of production, and energy savings potential for 11*
 186 *chemicals*

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
Chlorine/ Sodium Hydroxide	21,465/ 16,581	141	36	0.086	1,846	0.022	471
Nitrogen/Oxygen	69,609/ 58,287	99	18	0.010	1,296	0.002	236
Terephthalic Acid	2,217	16	17	0.094	209	0.100	223
Hydrogen	6,591	6	17	0.012	79	0.034	223
Propylene	31,057	42	11	0.018	550	0.005	144
Carbon Black	3,415	13	7	0.050	170	0.027	92
Ethylene Oxide	5,876	11	4	0.025	144	0.009	52
Methanol	2,024	10	4	0.065	131	0.026	52
TOTAL	358,757	1,152	563		\$ 15,081		\$ 7,371

187
 188 Worldwide, ethylene production consumes the most energy of all chemicals manufactured. In the
 189 U.S., ethylene is produced primarily from steam cracking of ethane and other NGL alkanes (e.g.,
 190 propane and butanes). The supply of ethane in the U.S. has increased significantly in concert with
 191 increasing production of shale gas, which typically has a higher concentration of NGL than
 192 conventional natural gas. In response, several chemical companies have announced plans to
 193 increase existing or build new ethylene capacity totaling 10 million metric tons/year by 2017,
 194 which would increase U.S. capacity by over 35%.²⁶ Consequently, ethylene is an important focus
 195 area for PI innovation.
 196

²⁴ A portion of the 563 TBtu/yr results from the potential energy savings of the implementation of best practices and state-of-the-art commercial equipment.

²⁵ Based on a simplified value of \$13.091 / MMBtu (calculated average of the industrial price of electricity and natural gas) EIA 2014: http://www.eia.gov/electricity/annual/html/epa_01_01.html and <http://www.eia.gov/dnav/ng/hist/n3035us3m.htm>

²⁶ B. Fallas and P. Pavlov, "Platts special report: petrochemicals, time to get cracking " McGraw-Hill Companies, Inc., New York, NY, USA2013.

197 Table 4 provides the 2010 Chemical Bandwidth study assessment of the technology readiness,
 198 market impact, relative cost, technical risk, productivity gain, and environmental impacts for PI
 199 technologies in the pipeline for the production of ethylene.

200

201 *Table 4 PI technologies applicable to the production of ethylene*²⁷

202

Technology	Technology Readiness	Market Impact	Relative Cost	Technical Risk	Productivity Gain	Environmental Benefits
Ethylene						
Microwave Enhanced Direct Cracking of Hydrocarbon Feedstock	M	H	L	M	H	H
Catalyst-Assisted Production of Olefins	M	H	M	M	M	M
Heat Integrated Distillation through use of Microchannel Technology	H	L	H	H	L	L
Hollow Fiber Membranes for Olefin/ Paraffin Distillation	L	M	M	M	M	M

H-High; M-Medium; L-Low

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205 Given the energy intensity of steam cracking, PI approaches to this process step could lead to
 206 significant energy savings. Microwave enhanced cracking of hydrocarbons is a new method for
 207 replacing the energy-intensive cracking furnace. In a conventional furnace, heat is transferred
 208 through the outer surface of coils or tubes. This technology takes advantage of microwaves which
 209 impart energy directly to the reactants and is expected to save 30%-50% energy consumption in
 210 the cracking process step^{28,29}. Another promising PI technology is catalyst-assisted production of
 211 olefins, highlighted in the **text box**, which provides a potential solution to downtime and efficiency
 212 losses caused by coking of the furnace walls.

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²⁷ Technologies and metrics are from: Energetics, "Chemicals Industry Updated Energy Bandwidth Study". 2013, U.S. DOE, EERE, AMO.

²⁸ S. Ng, C. Fairbridge, S. Mutyala, Y. Liu, J. R. Bélanger, and J. R. J. Paré, "Microwave-assisted conversion of ethane to ethylene," *Applied Petrochemical Research*, vol. 3, pp. 55-61, 2013.

²⁹ M. Fall, E. Wagner, F. Cabe, G. Eagleson, J. Carnahan, R. Lal, *et al.*, "Microwave Enhanced Cracking of Ethane for Ethylene Production " presented at the 24th Annual Ethylene Producers Conference Houston, Texas 2012.

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 CAMOL™ 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 furnace can be extended and its heat transfer can be improved. LyondellBasell, BASF, Qtech 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.

IMI project – should confirm, ask BASF for a graphic

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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 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 cross-cutting applicability.

Table 5 Current process and key unit operation commonalities of 12 chemicals

Chemical	Process Conditions			Cross-Cutting 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	✓					✓	✓		✓		
Propylene		✓			✓	✓		✓	✓		
Terephthalic Acid				✓	✓	✓				✓	
Carbon Black		✓		✓		✓				✓	
Ethylene Oxide			✓	✓	✓	✓		✓			

Methanol		✓	✓	✓	✓	✓		✓		
Hydrogen		✓		✓	✓	✓			✓	✓

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2.3 PI Technologies for Biorefining

An important strategy for reducing the carbon footprint of the chemical industry is to manufacture chemicals from biomass instead of petroleum or natural gas feedstock. To encompass this application area, we use the terminology of “biorefinery” 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.”³⁰

In one account, researchers³¹ foresee a future where 30% by weight of chemicals are produced from biomass by 2050 and postulate wide adoption of PI technologies within the new bio-based chemical industry. The authors explore the potential for these technologies by evaluating the benefits and challenges in several case studies. Results from their analysis are reprinted in Table 6. Among the PI technologies considered in their case studies are:

- 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 CO₂
- Microwave pyrolysis of biomass in CO₂ with simultaneous supercritical fluid extraction

Table 6 Assessment of PI technologies in the manufacture of chemicals from biomass

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J.P.M. Sanders et al. / Chemical Engineering and Processing 51 (2012) 117–136

Table 2

Scores of the case studies regarding the basic criteria for PI and specific challenges (+ means attractive; – means not attractive).

	Low capital	Efficient use of biomass/fossil	Safe	Compact/simple plant	Full use of biomass	Low transportation cost	Specific challenges
Propyleneglycol	+	+	+	+	–	–	E
H ₂	–	–	–	–	++	–	A B C D F G
Electrodialysis	+	++	+	+	–	+	E F
Cyanophycin	++	++	++	+	–	++	E F H
Isosorbide	++	++	++	++	–	+	A B C E F
Hydroxymethyl furfural	+	+	+	+	–	+	A B E G
Microwave/CO ₂ combination	+	+	+	+	–	+	E F

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- Separation of main components or derivatives from biomass at low capital and operational cost, with low energy use
- Reduction of the logistic costs, e.g. by increasing the (energy) density of biomass or to process close to the origin of the biomass resource
- Operations under A and B that can efficiently be performed at small scale, close to the fields, in order to avoid needless transport.
- Management of toxic production formation and trace elements (e.g., S, N, P, K)
- Identification of new platform chemicals that can be derived at sufficient volumes at high yields, low cost and high overall energy efficiencies
- Assessment of the most sustainable approach for producing base chemicals from biomass while maintaining sufficient food/feed supply (biomass with the lowest caloric value that can substitute the highest functionality value)
- Combination of separation and conversion in order to reduce costs and waste streams
- Treatment of (dilute) watery waste streams

³⁰ National Renewable Energy Laboratory (2009) “What is a biorefinery” <http://www.nrel.gov/biomass/biorefinery.html> (website visited 2/3/2015)

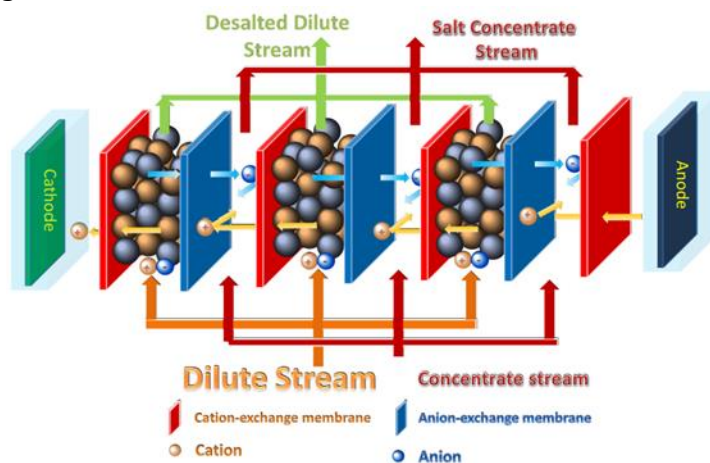
³¹ Sanders, J. P. M., J. H. Clark, G. J. Harmsen, H. J. Heeres, J. J. Heijnen, S. R. A. Kersten, W. P. M. Van Swaaij, and J. A. Moulijn. “Process intensification in the future production of base chemicals from biomass.” *Chemical Engineering and Processing: Process Intensification* 51 (2012): 117-136.

258 * This table will need to reconstructed, citing the Sanders et al publication.
 259
 260

261 A recent paper³² reviews a wide range of membrane technologies under development for the
 262 “bioeconomy”. Among the novel PI technologies described are membrane bioreactors for the
 263 production of ethanol, methane, hydrogen, acetic acid, and biodiesel. One example of an innovative
 264 membrane process, developed through a DOE sponsored program, is highlighted in the **text box**.
 265 Polymeric, ceramic, and hybrid membrane technologies are also being developed for the recovery
 266 of both chemical feedstocks from biomass and chemical products from mixed process streams. The
 267 processes reviewed in the paper have shown promising performance in laboratory and pilot
 268 experiments, though many of the applications are challenged by membrane fouling. Anaerobic
 269 membrane bioreactor technology was called out as particularly attractive for wastewater
 270 treatment, having been shown to require less energy and produce higher value effluents than other
 271 processes.
 272
 273

274 *Resin Wafer Electrodionization*

275
 276 Electrodeionization (EDI) is a modified version of electrodialysis (ED) that contains conductive ion
 277 exchange (IX) resin beads within the diluate compartment. EDI combines the advantages of ED and
 278 IX chromatography; however, it utilizes in-situ regeneration of the IX resin beads by a phenomenon
 279 known as “water splitting”. Water splitting on the surface of the IX resin beads regenerates the
 280 beads and ensures higher ionic conductivity within the diluate compartment. EDI outperforms ED
 281 with dilute solutions, where due to the limited ion concentration, ionic conductivity decreases and
 282 electrical energy is wasted in water splitting. In contrast, the conductive IX resin beads in EDI
 283 provide sufficient ionic conductivity,
 284 even with a dilute solution, and provide
 285 an efficient ion transport pathway
 286 through the IX resin beads. In
 287 conventional EDI, loose IX resin beads
 288 are used, however, the researchers at
 289 Argonne National Laboratory have
 290 improved the technology by using resin
 291 wafers (RW) to incorporate the loose ion
 292 exchange resin. The technology offers
 293 enhanced fluid and flow distribution,
 294 higher conductivity, superior pH control,
 295 ease of materials handling and system
 296 assembly, and a porous solid support for incorporation of catalysts, biocatalysts, and other
 297 adjuvants. RW-EDI is used for production and recovery of biobased chemicals, especially organic
 298 acids from fermentation broth, post-transesterification glycerin desalting, conditioning of biomass
 299 hydrolysate liquor, and for CO₂ capture from flue gas.



300

³² He, Y., Bagley, D. M., Leung, K. T., Liss, S. N., & Liao, B. Q. (2012). Recent advances in membrane technologies for biorefining and bioenergy production. *Biotechnology advances*, 30(4), 817-858.

301
302
303 In biomass to ethanol plants, two separation challenges provide opportunity space for PI
304 technologies³³. First, fermentation inhibitors need to be removed from the lignocellulosic feed after
305 the hemicelluloses have been extracted. PI technologies being developed for this detoxification
306 step include extractive fermentation, membrane pervaporation-bioreactor, and vacuum membrane
307 distillation-bioreactor.

308
309 Recovery of the fuel-grade ethanol from water is the second separation challenge. This separation is
310 energy intensive because of the low starting concentration of ethanol (5-12 wt% ethanol) and the
311 water-ethanol azeotrope that forms at 96.5 wt% ethanol concentration. The separation is typically
312 undertaken in two processing steps: conventional distillation concentrating the solution to 80-85
313 mol% ethanol followed by extractive or azeotropic distillation for dehydration. Novel low energy
314 intensive technologies under development include extractive distillation with ionic liquids or
315 hyperbranched polymers³⁴. Other energy efficient technologies, including pervaporation and
316 molecular sieve absorption, have been found to be constrained to low capacity applications³⁵.
317 Evaluating a PI approach using Aspen Plus simulations, researchers estimate energy savings of 10-
318 20% could be achieved by replacing an optimized two column extractive distillation with a single
319 divided wall column (DWC) or 20% savings by replacing an optimized two column azeotropic
320 distillation with a single DWC³⁶. The researchers note that reported energy savings of 25-40%
321 from other studies are based on comparisons of the PI alternatives with non-optimized two column
322 designs.

323
324 PI technologies are also being explored to reduce the residence times, operating costs, and energy
325 consumption of producing biodiesel via transesterification of vegetable oils and animal fats. A
326 recent review article³⁷ describes experimental and commercial PI technologies. Table 7 provides
327 comparative information on the performance of these PI technologies. Centrifugal contactor
328 technology, originally developed through DOE sponsored research on the selective recovery of
329 metal elements from spent nuclear fuel, has been successfully applied to biodiesel production. In
330 this continuous process, the centrifugal contactor equipment hosts both the reaction of
331 triglycerides with alcohol and the separation of product biodiesel from byproduct glycerol,
332 achieving efficient mixing and precisely controlled residence times.³⁸

333
334

³³ Huang, H. J., Ramaswamy, S., Tschirner, U. W., & Ramarao, B. V. (2008). A review of separation technologies in current and future biorefineries. *Separation and Purification Technology*, 62(1), 1-21.

³⁴ Huang, H. J., Ramaswamy, S., Tschirner, U. W., & Ramarao, B. V. (2008). A review of separation technologies in current and future biorefineries. *Separation and Purification Technology*, 62(1), 1-21.

³⁵ Frolkova, A. K., and V. M. Raeva. "Bioethanol dehydration: state of the art." *Theoretical Foundations of Chemical Engineering* 44, no. 4 (2010): 545-556.

³⁶ Kiss, Anton A., and David J. Suszwalak. "Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns." *Separation and Purification Technology* 86 (2012): 70-78.

³⁷ Qiu, Zheyang, Lina Zhao, and Laurence Weatherley. "Process intensification technologies in continuous biodiesel production." *Chemical Engineering and Processing: Process Intensification* 49, no. 4 (2010): 323-330.

³⁸ ORNL, (2011) factsheet "Manufacturing Biodiesel from Triglycerides" UT-B IDs 200702012, 200701972, 200802186.

335 **Table 7 PI technologies for the production of biodiesel from vegetable oils and animal fats**

Table 1
Comparison of process intensification technologies for continuous biodiesel production with conventional stirred tank reactors.

	Residence time	Energy efficiency (g/J)	Operating and capital cost	Temperature control	Current status
Static mixer	~30 min	14.9–384 [30]	Low	Good	Lab scale
Micro-channel reactor	28 s–several minutes	0.018 [8]	Low	Good	Lab scale
Oscillatory flow reactor	30 min	N/A	Low	Good	Pilot plant
Cavitation reactor	Microseconds–several seconds	1×10^{-4} to 2×10^{-4} (hydrodynamic cavitation), 5×10^{-6} to 2×10^{-5} (acoustic cavitation)	Low	Good	Commercial scale
Spinning tube in tube reactor	<1 min	N/A	Low	Good	Commercial scale
Microwave reactor	Several minutes	~0.038 L/kJ [24]	Low	Good	Lab scale
Membrane reactor	1–3 h	N/A	Lower	Easy	Pilot plant
Reactive distillation	Several minutes	~ 1.6×10^{-6} [43]	Lower	Easy	Pilot plant
Centrifugal contactor	~1 min	N/A	Lower	Easy	Commercial scale

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337 * Reconstruct, cite Qui et al publication.

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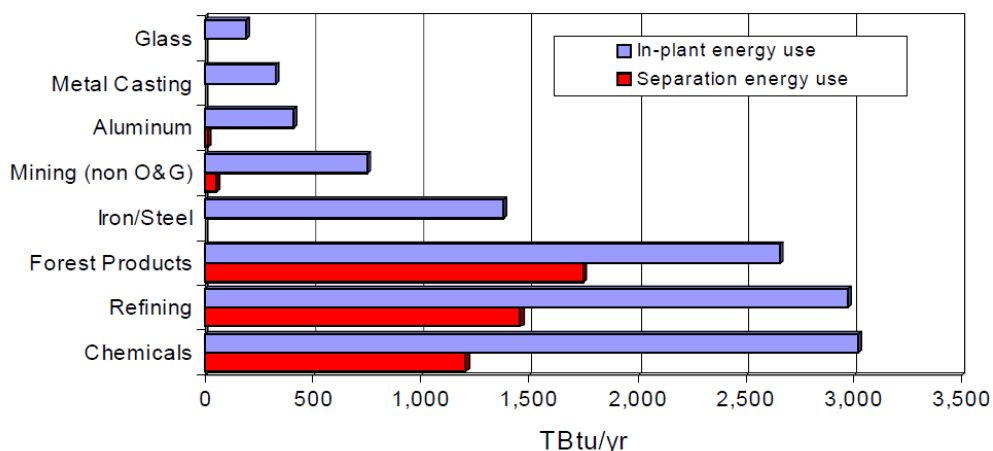
340 2.4 PI Technologies for Separations

341

342 One cross-cutting area in which PI technologies could be particularly impactful is in separations.
343 Separation technologies are estimated to consume about 22% of in-plant energy use in the U.S.
344 industrial sector.³⁹ As shown in Figure 5, separation energy-intensive manufacturing industries
345 include chemicals, petroleum refining, and forest products⁴⁰.

346

Figure B: In-plant and Separation Energy Use for Energy-Intensive Industries



Source: Appendix A, Table A.2

347

348 *Figure 5 In-plant and separation energy use for energy-intensive industries*

349 **[Need to redraw. Is there an update? Figure extracted from BSC – ORNL 2005 paper.]**

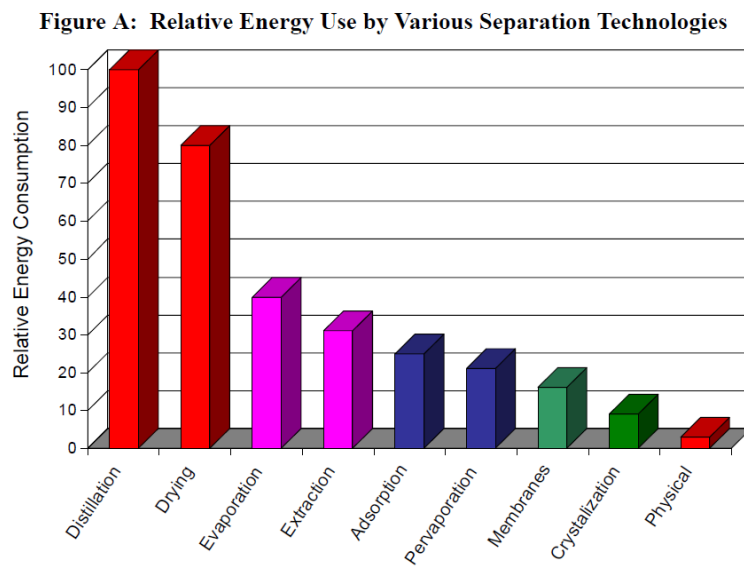
350

351 Many types of separation technologies are currently used in industry, falling broadly into the
352 categories of distillation, drying, evaporation, extraction, adsorption, pervaporation, membranes,

³⁹ BCS, Incorporated and Oak Ridge National Laboratory (2005). Materials for Separation Technologies: Energy and Emission Reduction Opportunities. Report prepared for the U.S. DOE, Industrial Technologies Program.

⁴⁰ BCS, Incorporated and Oak Ridge National Laboratory (2005). Materials for Separation Technologies: Energy and Emission Reduction Opportunities. Report prepared for the U.S. DOE, Industrial Technologies Program.

353 crystallization, and physical separations (e.g. flotation, screening, magnetic separation). As shown
 354 in Figure 6, distillation and drying consume a large portion of the industrial energy use for
 355 separations.
 356



357
 358 *Figure 6 Relative energy use by various separation technologies*

359 **[Need to redraw. Is there an update? Figure extracted from BSC - ORNL 2005 paper.]**

360

361 Materials and process development strategies for reducing separation energy include:

- 362 • Replacing high-energy technologies (e.g., distillation, drying, and evaporation) with low-
 363 energy technologies (e.g., extraction, absorption, adsorption, membrane separations,
 364 crystallization, and physical-property based operations)
- 365 • Adopting process intensification strategies (e.g., hybrid separations, reactive separations,
 366 and alternative energy sources - centrifugal field, ultrasound, microwave, electric fields,
 367 microwave)

368

369 A study⁴¹ of separation applications in petroleum refining and ten chemical processes identified
 370 several high energy distillations, which could yield energy savings if replaced with membrane
 371 separations, extraction, absorption, and hybrid systems:

- 372 • Separation of olefin-paraffin streams: e.g., ethylene/ethane, propylene/propane,
 373 butadiene/butanes, and styrene/ethylbenzene
- 374 • Recovery of organics that azeotrope with water from aqueous solutions: e.g., ethanol,
 375 isopropanol, butanol
- 376 • Recovery of dilute organics from dilute water solutions: e.g. acetic acid, ethylene glycol,
 377 methanol
- 378 • Cryogenic air separation
- 379 • Polyol separations: e.g., ethylene glycol/propylene glycol, ethylene glycol/diethylene glycol
- 380 • Isomer separations: e.g., p-xylene/mixed xylenes, n-paraffins from isoparaffins

381

⁴¹ BCS, Incorporated and ORNL. 2005. Materials for Separation Technologies: Energy and Emission Reduction Opportunities. May 4, 2005.

382 The study also identified energy savings opportunity for developing membrane separations to
 383 replace evaporation processes in the production of caustic soda and phosphoric acid. Table 8
 384 provides a summary of the energy savings estimated to be possible if more energy efficient
 385 separations technologies, including PI technologies, are deployed in these select chemical
 386 processes.

387
 388
 389

Table 8 Energy savings potential for new separation technologies, including PI technologies

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%

390 Adapted from data in the 2005 separations study ⁴²

391

3. Program Considerations to Support R&D

392
 393

394 With tens of thousands of chemicals produced in the U.S. and hundreds of industrial processes to
 395 produce these chemicals, considerable potential exists for near- and long-term energy and carbon
 396 emission savings through the development of PI technologies and novel processes. RD&D
 397 investment in PI technologies is expected to have wide ranging applicability across the chemical
 398 industry as well as other industries. Metrics of successful PI RD&D will encompass cost reduction,
 399 energy efficiency, carbon efficiency, and waste reduction compared to state of the art technologies.
 400 An overarching goal is to apply PI methods to develop smaller, modular equipment, which deliver
 401 50-70% reductions in waste, energy use, and capital and operating costs when compared to the
 402 existing state of the art processes. Key focal areas for RD&D are:

403

- 404 • *PI Equipment*: physical hardware and their operating parameters providing improved
 405 chemicals processing environment and profiles - such as novel mixing, heat-transfer and
 406 mass-transfer technologies, and devices
- 407 • *PI Methods*: improved or novel chemical processes enabled by equipment - such as new or
 408 hybrid separations, integration of reaction and separation steps, improved heat exchange -
 409 or phase transition (multifunctional reactors), the use of a variety of energy sources (light,
 410 ultrasound, magnetic fields), and new process-control methods (intentional non-
 411 equilibrium-state operation)
- 412 • *PI Supporting Practices*, such as improved manufacturing processes for new equipment and
 413 improved systems integration, common standards and interoperability, modular systems
 414 design and integration, supply chain development and flexibility, workforce training, and
 415 financing.

⁴² BCS, Incorporated and ORNL. 2005. Materials for Separation Technologies: Energy and Emission Reduction Opportunities. May 4, 2005.

416
417 An important RD&D goal for PI is to provide low energy alternatives to replace energy intensive
418 distillation and evaporation process steps. Many of these PI solutions require separation agents, for
419 example, solvents, sorbents, ion exchange resins, molecular sieves, and membranes. These agents
420 need to be developed specifically for each application because separation efficiencies depend on the
421 chemical and physical interactions between the separation agent and the components in the
422 process stream, which differ application to application. To promote commercial deployment of
423 these technologies, RD&D is needed to improve the performance of separation agents in the areas
424 of:

- 425 • **selectivity** required to achieve the desired separation;
- 426 • **throughput** (flux, loading capacity, etc.) required for reasonable system economics;
- 427 • sufficient **durability** to maintain optimum performance under the harsh industrial
428 environments (i.e., severe pressures, temperatures, corrosiveness, fouling, etc.); and
- 429 • sufficient **economies-of-scale incentive** to be considered an alternative to established
430 technologies in large-volume industrial processes.

431
432 The DOE’s agenda for PI RD&D is evolving and will be informed through public-private dialogue.
433 During a multi-stakeholder workshop sponsored by the National Science Foundation (NSF),
434 industry representatives identified three favorable conditions for adoption of PI technologies:⁴³

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

440
441 High potential application areas identified by the industry group at the NSF sponsored workshop
442 include⁴⁴:

- 443 • Chemical industries as an approach to improving reaction and separation efficiencies and
444 increasing plant capacities
- 445 • Biorefining, being dominated by new construction and with distributed supply chains, may
446 be amenable to adoption of PI technologies for smaller scale, distributed production
- 447 • Stranded natural gas separations and conversion
- 448 • Water management in remote locations and distributed manufacturing sites
- 449 • Carbon management for power generation to replace traditional technologies that do not
450 scale well with low pressure drops

451
452 The *European Roadmap for Process Intensification* (2008) provides insights on RD&D strategies.
453 First, the roadmap recognizes that while overall cost competitiveness is a major focus for
454 innovation of PI technologies, the benefits sought from PI implementations vary from chemical to
455 chemical. For large volume production of petrochemicals and bulk chemicals, reducing energy costs
456 and environmental impact are significant drivers of technology innovation. Conversely, energy
457 costs make up a smaller fraction of the production costs for specialty chemicals and

⁴³ Robinson, S. 2014. Private communication: notes from the National Science Foundation Sponsored Process Intensification Workshop, September 30 – October 1, 2014, Virginia Tech Executive Briefing Center.

⁴⁴ Robinson, S. 2014. Private communication: notes from the National Science Foundation Sponsored Process Intensification Workshop, September 30 – October 1, 2014, Virginia Tech Executive Briefing Center.

458 pharmaceuticals. In these industries, achieving improvements in selectivity, yield, and processing
459 time are more important to their cost competitiveness.

460

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

468

469 Enabling technologies for successful industrialization of PI technologies noted in the European
470 roadmap are:

- 471 • In-situ measurement and analysis methods to better understand molecular level kinetic and
472 thermodynamic characteristics of chemical processes
- 473 • Faster, more robust, non-linear numerical modeling of chemical processes
- 474 • Process control systems of modular equipment

475

476 Process integration introduces unique process control challenges.⁴⁵ In these multi-functional
477 systems, fewer degrees of freedom are available for control than would be with divided single-
478 purpose process steps. The desirable operating ranges for multi-functional systems are often
479 narrower, yet due to smaller spatial and temporal scales, the dynamics are more extreme. The
480 development of customized on-line control algorithms based on fast and reliable process models
481 are needed to address these challenges.

482

483 **4. Risk, Uncertainty, and Other Considerations**

484

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

494

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

⁴⁵ Nikačević, N. M., Huesman, A. E., Van den Hof, P. M., & Stankiewicz, A. I. (2012). Opportunities and challenges for process control in process intensification. *Chemical Engineering and Processing: Process Intensification*, 52, 1-15.

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In conclusion, R&D investment to advance PI technologies would have:

- High impact – energy efficiency potential for high-value U.S. industries including chemicals, mining, oil & gas extraction, petroleum refining, waste & recycling, biofuels, and power generation
- Additionality – mature industries with large, capital intensive assets focus R&D on improving existing technologies and may be reluctant to invest in transformative technologies
- Openness – involvement of stakeholders in the R&D process
- Enduring economic benefit – innovative technologies will enable customized plants, increased localized production, greater utilization of U.S. feedstocks, and more efficiency in serving U.S. demand
- Proper role of government – maintenance of a high level vision for the development and widespread applicability of innovative technologies and promotion of shared requirements, technologies, and goals that result in collaborative, jointly-beneficial research

517 **5. More information & references on Case Studies**

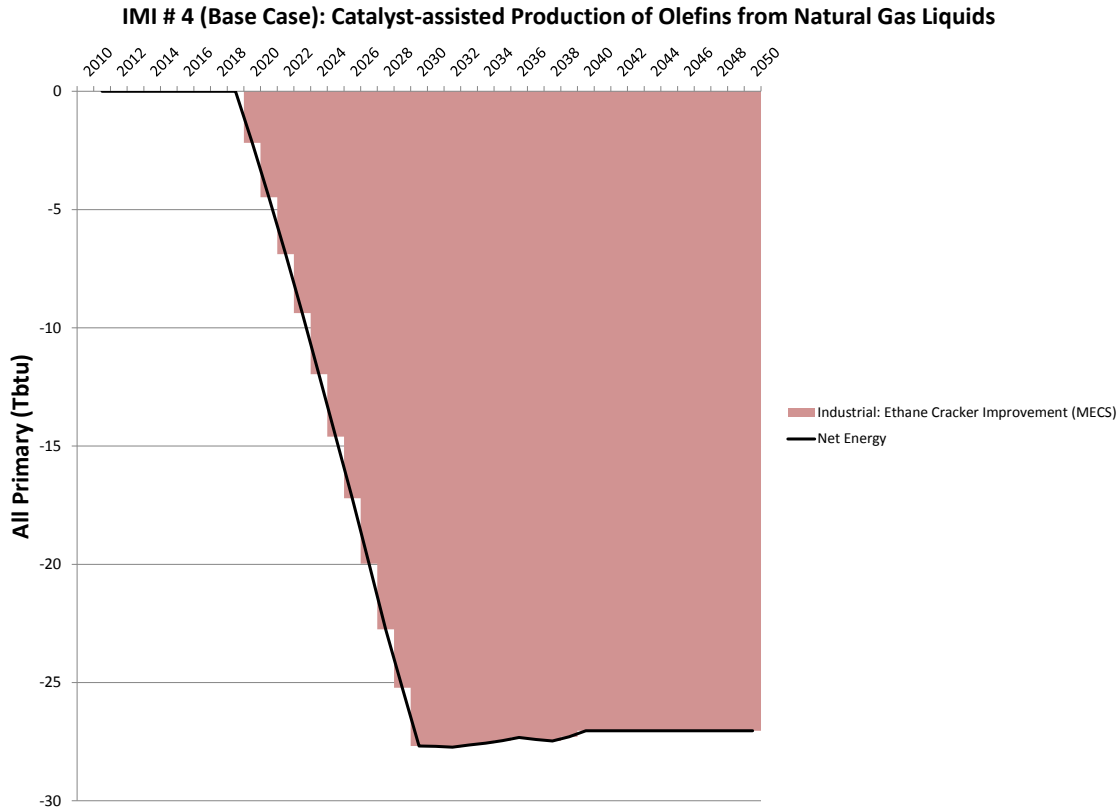
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Catalyst assisted production of olefins from natural gas liquids

Ethylene, an important olefin, is a key building block in the production of numerous chemicals and polymers and the largest volume organic chemical produced in the United States and the world today. Ethylene also has one of the highest overall energy consumption totals compared to the production of other chemicals across the U.S. chemical industry. The production of ethylene from ethane is expected to grow significantly due to the exploitation of vast reserves of shale gas in the U.S.

Most ethylene (over 98%) is produced through a 40-year-old steam cracking process. In this process, hydrocarbons (either a natural gas liquids (NGLs) or naphtha feedstock) are pyrolyzed at temperatures of 800°C–900°C and then cooled. Ethylene is separated from the resulting complex mixture by compression and distillation. 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 halting ethylene production to remove coke from the furnace walls.

Using a conventional steam cracker, this project will develop and apply a novel catalytic coating on internal surfaces of the coils where ethane is converted at extremely high temperatures to ethylene. The catalyst contained in the coating catalyzes the oxidation of the carbon on the surface, greatly reducing coke formation and its associated problems. Less coke formation within the coils contributes to longer run times and lower decoking frequency, leading to savings in energy and corresponding greenhouse emissions. Results from prototype tests using early generations of the catalytic coating and naphtha feedstock will serve as a good starting point, but this project will focus on ethylene produced from ethane (a NGL) feedstock. Researchers will eventually conduct full-scale prototype testing under real-world operating conditions.



547
548 **LIGHTEN-UP Case Study Results (Mid) – Catalyst-Coated Coils for Steam Cracking Ethylene**
549 **Production**
550

551 References:
552 BASF, "CAMOL™ Catalytic Coatings for Steam Cracker Furnace Tubes," BASF Canada 2012.
553 (06/15). CAMOL™ Catalytic Coating Available: <http://www.basf-qtech.com/p02/USWeb-Internet/basf-qtech/en/content/microsites/basf-qtech/prods-inds/camol>
554
555 DOE. (2012, 06/08). *Innovative Manufacturing Initiative Project Descriptions*. Available:
556 http://www1.eere.energy.gov/manufacturing/pdfs/imi_project_descriptions.pdf
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559 **Resin Wafer Electrodionization**

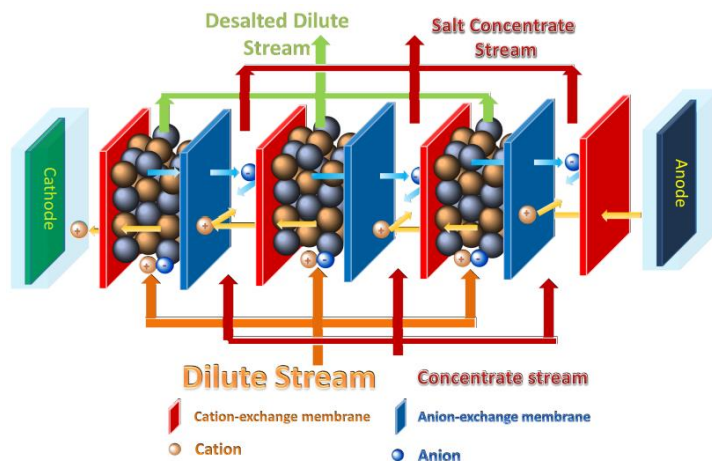
560 Electrodeionization (EDI) is a modified version of electrodialysis (ED) that contains conductive
561 ion exchange (IX) resin beads within the diluate compartment. EDI combines the advantages of
562 ED and IX chromatography; however, it utilizes in-situ regeneration of the IX resin beads by a
563 phenomenon known as “water splitting”. Water splitting on the surface of the IX resin beads
564 regenerates the beads and ensures higher ionic conductivity within the diluate compartment. EDI
565 outperforms ED with dilute solutions, where due to the limited ion concentration, ionic
566 conductivity decreases and electrical energy is wasted in water splitting. In contrast, the
567 conductive IX resin beads in EDI provide sufficient ionic conductivity, even with a dilute
568 solution, and provide an efficient ion transport pathway through the IX resin beads. In
569 conventional EDI, loose IX resin beads are used, however, the researchers at Argonne National
570 Laboratory have improved the technology by using resin wafers (RW) to incorporate the loose

571 ion exchange resin. The modified platform is called RW-EDI. The technology offers enhanced
 572 fluid and flow distribution, higher conductivity, superior pH control, ease of materials handling
 573 and system assembly, and a porous solid support for incorporation of catalysts, biocatalysts, and
 574 other adjuvants. RW-EDI is used for production and recovery of biobased chemicals, especially
 575 organic acids from fermentation broth, post-transesterification glycerin desalting, conditioning of
 576 biomass hydrolysate liquor, and for CO₂ capture from flue gas. Argonne deploys three different
 577 ED stack sizes to design experiments and evaluate performance from fundamental and
 578 exploratory scale research through pilot-scale and field deployment. A small stack (14 cm²
 579 surface area) is used for proof of concept experiments, which is then scaled up to a TS2 stack
 580 (195 cm² surface area) for process optimization and more rigorous studies. At the pilot scale
 581 (1700 cm² surface area) extended campaigns are conducted to evaluate potential for
 582 commercialization.

583 Viewed very simplistically, the design of an RW-EDI device is like a horizontal stack of
 584 sandwiches with a negative electrode at the left end of the stack and a positive electrode at the
 585 right end of the stack. As a result of that attraction that positive ions have for negative charges,
 586 and vice versa, the most mobile negative ions tend to want to move right, and the most mobile
 587 positive ions tend to want to move left. In order to enable that mobility of the ions to move left
 588 or right according to their respective preferences, the layers of the sandwiches are made up of
 589 membranes or wafers that are microscopically porous; only water and individual ions *can* pass
 590 through. Each membrane is specialized either to allow anions to pass through, or to allow
 591 cations to pass through, but not both. Sugar molecules and other larger uncharged molecules
 592 cannot pass through.

593 The next detail of the design is that the feed stream being fed to the RW-EDI device in order to
 594 be cleaned up is only fed to every other layer. In between are the layers where the concentrate
 595 stream that is *receiving* the salt is flowing. These devices are sized, and the flow rate is
 596 optimized, for the particular process conditions and performance specifications, so that by the
 597 time the feed stream has flowed through the device, the desired extent of separation has
 598 occurred.

599 Applying the example of dextrose syrup desalination to the schematic diagram below, the salty
 600 syrup flows in at the bottom, and the desalted syrup flows out of the top (through half the
 601 channels), while clean water flows in at the bottom, and the salty water flows out of the top
 602 (through the other half of the channels).



603

604

605 In this multi-module pilot-scale assembly, the fluid flow equipment and power supply are scaled
 606 up, reflecting the larger (larger cross section and more layers) module. In the pilot system
 607 pictured here, a single module with a cross section of 2000 cm² and 20 “cell pairs,” the technical
 608 term for the sandwich layers in a module. At the pilot scale, it is already possible to envision a
 609 commercial installation, in which a single RW-EDI module consists of 100+ layers, and a battery
 610 of multiple RW-EDI modules operate in parallel, installed in such a manner that individual
 611 modules can be taken off-line for repair or replacement, while the assembly as a whole remains
 612 on line and continues processing.

613 The manufacture of RW-EDI modules, construction of the bench-scale and pilot-scale RW-EDI
 614 processing units, and operation of these systems have all been carried out. The system has been
 615 used in campaigns up to 2000 hours. It has been deployed at the lab and pilot scale in industrial
 616 facilities. It has been operated at the laboratory in remote environmental projects.

617 Argonne licensed the technology to Nalco Company ([http://www.nalco.com/news-and-
 618 events/5167.htm](http://www.nalco.com/news-and-events/5167.htm)). Subsequently Nalco was acquired by Ecolab. Ecolab is considering various
 619 market opportunities. In parallel, Argonne has conducted several privately-funded projects to
 620 assess specific customer separations needs. Argonne is evaluating a business plan to create a
 621 spin-off to serve those customer markets.

622

623 Publications

- 624 1) S. Datta, Y. P. J. Lin and S. W. Snyder “Current and emerging separation technologies used in
 625 biorefining”, in *Advances in Biorefineries*, K. Waldron, Ed., Woodhead Publishing Series in Energy,
 626 Cambridge UK, **2014** 112-151, DOI: 10.1533/9780857097385.1.112
 627 ([http://books.google.com/books?hl=en&lr=&id=JQKjAgAAQBAJ&oi=fnd&pg=PA112&ots=GQkE
 628 PmBt4s&sig=qcBZ0Pfl-QRDcTutmNQRW0LRYwM#v=onepage&q&f=false](http://books.google.com/books?hl=en&lr=&id=JQKjAgAAQBAJ&oi=fnd&pg=PA112&ots=GQkEPmBt4s&sig=qcBZ0Pfl-QRDcTutmNQRW0LRYwM#v=onepage&q&f=false)).
- 629 2) S. Datta, M. P. Henry, Y.J. Lin, A.T. Fracaro, C.S. Millard, S.W. Snyder, R.L. Stiles, J. Shah, J.
 630 Yuan, L. Wesoloski, R.W. Dorner, W.M. Carlson “Electrochemical CO₂ capture using resin-wafer
 631 electrodeionization (RW-EDI)”, *Industrial and Engineering Chemistry Research* **2013**, 52(43),
 632 15177-15186 (<http://pubs.acs.org/doi/abs/10.1021/ie402538d>).
- 633 3) S. Datta, S.W Snyder, D.J. Schell, C.S Millard, S.F. Ahmad, M.P. Henry, P. Gillenwater, A.T
 634 Fracaro, A. Moradia, Z.P. Gwarnicki, Y.J. Lin “Removal of Acidic Impurities from Corn Stover
 635 Hydrolysate Liquor by Resin Wafer based Electrodeionization (RW-EDI)”, *Industrial and
 636 Engineering Chemistry Research* **2013**, 52(38),13777–13784 (<http://dx.doi.org/10.1021/ie4017754>)
- 637 4) R.N. Gurram, S. Datta, Y.J. Lin, S.W. Snyder, T.J. Menkhaus, “Removal of Enzymatic and
 638 Fermentation Inhibitory Compounds from Biomass Slurries for Enhanced Biorefinery Process
 639 Efficiencies”, *Bioresource Technology*, **2011**, 102, 7850–7859
 640 (<http://dx.doi.org/10.1016/j.biortech.2011.05.043>)
- 641 5) M.B. Arora, J.A. Hestekin, S.W. Snyder, E. St. Martin, M. Donnelly, C. S. Millard, Y.P. Lin “The
 642 Separative Bioreactor: A Continuous Separation Process for the Simultaneous Production and Direct
 643 Capture of Organic Acids, *Separations Science and Technology*, **2007**, 2 (11): 2519-2538

644 Patents

- 645 1. Y.J. Lin, S.W. Snyder, M.P. Henry, S. Datta "Internal Gas and Liquid Distributor for an
646 Electrodeionization Device", U.S. Patent Application 20130233715
647 2. Y.J. Lin, S.W. Snyder, S. Datta, M.C. Trachtenberg, R. Cowen "Carbon Dioxide Capture Using
648 Resin-Wafer Electrodeionization", U.S. Patent 8,864,963
649 3. S.W. Snyder, Y.J. Lin, M. Urgun-Demirtas "Methane Production Using Resin-Wafer
650 Electrodeionization", U.S. Patent 8,679,314
651 4. E.J. St. Martin, Y.J. Lin, "Bioprocess utilizing carbon dioxide and electrodeionization", U.S. Patent
652 8,580,096
653 5. Y.J. Lin, E.J. St. Martin, Electrochemical method for producing a biodiesel mixture comprising fatty
654 acid alkyl esters and glycerol", U.S. Patent 8,507,229
655 6. Y.J. Lin, S.W. Snyder, S. Datta, M.C. Trachtenberg, R. Cowen "Carbon Dioxide Capture Using
656 Resin-Wafer Electrodeionization", U.S. Patent 8,506,784
657 7. Y.P. Lin, S.W. Snyder, E. St. Martin, "Retention of Counterions in the Separative Bioreactor", U.S.
658 Patent 8,007,647
659 8. T. Rajh, Y. J. Lin, N. M. Dimitrijevic, S. W. Snyder, N. Sather, "Integrated Device and Substrate for
660 Separating Charged Carriers and Reducing Photocorrosion: Method for the Photoelectrochemical
661 Production of Electricity and Photocatalytic Production of Hydrogen", 2007 U.S. Patent 7,981,261
662 9. M.B. Arora, J.A. Hestekin, Y.P. Lin, E. J. St. Martin, S.W. Snyder, "Method of stripping genetically
663 tagged biomolecules from porous solid ion exchange wafer", U.S. Patent 7,799,548
664 10. Y.J. Lin, M. P. Henry, S.W. Snyder, E. St. Martin, M. B. Arora, L. de la Garza, "Devices Using Resin
665 Wafers and Applications Thereof", U.S. Patent 7,507,318, PCT filed in Brazil, India, Australia.
666 11. Y.J. Lin, M. P. Henry, S.W. Snyder, "Electronically and Ionically Conductive Porous Material and
667 Method for Manufacture of Resin Wafers Therefrom", U.S. Patent 7,452,920 and PCT.
668 12. M.B. Arora, J.A. Hestekin, Y.P. Lin, E. J. St. Martin, S.W. Snyder, "Porous Solid Ion Exchange
669 Wafer for Immobilizing Biomolecules", U.S. Patent 7,306,934
670 13. Y.J. Lin, M.P. Henry, J. Hestekin, S.W. Snyder, E. St. Martin, "Single-Stage Separation and
671 Esterification of Cation Salt Carboxylates Using Electrodeionization", U.S. Patent 7,141,154.
672 14. Y.J. Lin, J.A. Hestekin, M.B. Arora, E. J. St. Martin, "Electrodeionization method", U.S. Patent
673 6,797,140.
674 15. R. Datta, Y. Lin; D. Burke, S.P. Tsai, "Electrodeionization substrate, and device for
675 electrodeionization treatment", U.S. Patent 6,495,014.
676
677

Awards

- 678 2006 R&D 100 Award
679 2012 Federal Laboratory Consortium Award for Excellence in Technology Transfer
680

AMO-supported Velocys R&D project

682 Velocys⁴⁶, incorporated in 2001 as a spin-off from Battelle to commercialize microchannel process
683 technology developed at the Pacific Northwest National Laboratory. AMO supported the
684 microchannel reactor research that successfully developed reactions producing 20x the yield of a
685 conventional slurry reactor. The modular reactors for steam methane reforming and FT synthesis
686 consist of parallel arrays of microchannels with dimensions in the range of 0.1 to 5.0 mm. Typical
687 design throughputs are 15-150 MSCFD natural gas producing 1,500 to 10,000 barrels of liquid
688 product. Velocys has entered a joint venture with Waste Management, NRG Energy, and Ventech
689 Engineers, for a commercial plant under construction in Oklahoma City, OK, and expected to startup
690 in 2016.

⁴⁶ Tonkovich, A. L., Kai Jarosch, Sean Fitzgerald, Bin Yang, David Kilanowski, Jeff McDaniel, and Tad Dritz. "Microchannel Gas-to-Liquids for Monetizing Associated and Stranded Gas Reserves." (2011).

691
692 Challenges in the commercialization include fabrication of the microchannel reactors, design of feed
693 and product manifolds to distribute and control flows to and from multiple microchannels, and
694 developing scalable designs for multiple microchannel devices integrated into chemical plants.⁴⁷
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696 Velocys is also applying its microchannel technology to biomass-to-liquids (BTL) and is pursuing an
697 opportunity to build a 1,100 bpd BTL plant supported by the U.S. DoD and DOE.
698 Since its start-up, more than \$300 million has been invested in development of small scale gas-to-
699 liquids technology
700

⁴⁷ Tonkovich, A., D. Kuhlmann, A. Rogers, J. McDaniel, S. Fitzgerald, R. Arora, and T. Yuschak. "Microchannel technology scale-up to commercial capacity." *Chemical Engineering Research and Design* 83, no. 6 (2005): 634-639.