

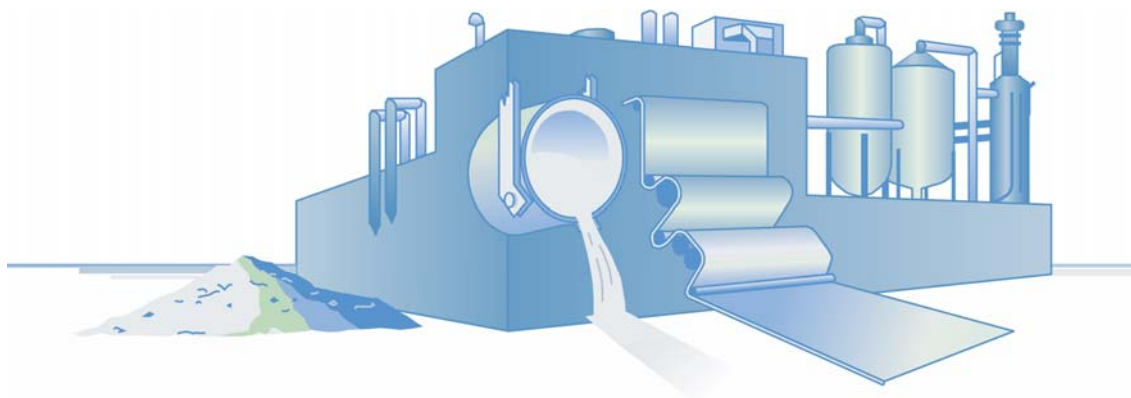


**U.S. Department of Energy**  
**Energy Efficiency**  
**and Renewable Energy**

Bringing you a prosperous future where energy  
is clean, abundant, reliable, and affordable

# Chemical Bandwidth Study

Exergy Analysis: A Powerful Tool for  
Identifying Process Inefficiencies in the  
U.S. Chemical Industry



## Industrial Technologies Program

DRAFT Summary Report  
December 2006

Study conducted for the U.S. Department of Energy  
by JVP International, Incorporated and Psage Research, LLC  
Summary report prepared by Energetics Incorporated

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# Preface

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

ITP's Chemicals subprogram supports R&D relevant to the chemical industries. This study, which focuses on energy efficiency in the chemical industry, was initiated in FY2003 by Dr. Dickson Ozokwelu, Lead Technology Manager, ITP Chemicals subprogram, to help guide research decision-making and ensure that Federal funds are spent effectively. The study was overseen by both Dr. Ozokwelu and Dr. Joseph Rogers of the American Institute of Chemical Engineers (AIChE), with analytical studies performed by Psage Research, LLC and JVP International. The intent of the study is to apply energy and exergy analysis to selected chemical manufacturing processes to determine sources of inefficiency and to locate potential process-specific areas for energy recovery.

Front-end analysis was performed by Psage Research, LLC, using various software tools developed by Psage, Jacobs Engineering of the Netherlands, and AspenTech (Aspen Plus, and the AspenPEP library, a collaboration between AspenTech and SRI's PEP program). JVP International reviewed and further analyzed the results to prepare recommendations for future research.

The study provides valuable insights into potential targets for the development and adoption of advanced, energy-efficient technologies in chemicals manufacture. It will be an important tool at DOE for assessing future directions in chemicals R&D conducted under the ITP Chemicals subprogram.

*This summary is a condensation of a much larger work, and does not contain the comprehensive data sets generated in that effort. Questions concerning the original work or this summary report can be directed to the authors shown below.*

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*This report is available on-line at [www.eere.energy.gov/industry/chemicals](http://www.eere.energy.gov/industry/chemicals).*



# Table of Contents

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## Introduction

Overview of Chemical Industry Energy Use .....	1
Objectives of the Analysis .....	2

## Methodology

Energy Bandwidth Analysis .....	3
Introduction to Exergy Analysis .....	5
Selection of Chemical Processes .....	8
Energy and Exergy Modeling Methodology.....	11
Model Integration.....	11
Unit Processes and Equipment.....	12
Model Output.....	13
Limitations of the Approach.....	14

## Summary of Results

Overview of Results.....	15
Trends Observed in the Bandwidth Analysis Results.....	17
Chemical Bandwidth Profiles .....	19
Ethylene .....	20
Chlorine .....	21
Sulfuric Acid .....	22
Hydrogen .....	22
Ammonia.....	23
Ethylene Oxide.....	23
Propylene.....	24
Terephthalic Acid.....	24
Carbon Black.....	25
Methyl Tert-Butyl-Ether (MTBE).....	25
Methanol.....	26
Acrylonitrile (ACN).....	27
Ethylene Dichloride.....	28
Formaldehyde.....	28
Phenol.....	29
Nitric Acid.....	30
Propylene Oxide.....	30
Soda Ash .....	31
p-Xylene .....	31
Styrene .....	32
Ethylbenzene .....	33
Ethylene Glycol.....	34
Vinyl Chloride .....	34
Methyl Methacrylate .....	35
Carbon Dioxide.....	35
Oxygen.....	36
Nitrogen.....	36
Urea.....	37
Phosphoric Acid.....	37
Vinyl Acetate (VAM).....	38
Ammonium Nitrate.....	38

<i>Caprolactam</i> .....	39
<i>Acetic Acid</i> .....	39
<i>Hydrochloric Acid</i> .....	40
<i>Isobutylene</i> .....	40
<i>Cumene</i> .....	41
<i>Aniline</i> .....	42
<i>Nitrobenzene</i> .....	42
<i>Ammonium Sulfate</i> .....	43
<i>Butadiene</i> .....	43
<i>bisPhenol A</i> .....	44
<i>Cyclohexane</i> .....	44
<i>Isopropyl Alcohol</i> .....	45
<i>Methyl Chloride</i> .....	45
Energy and Exergy Losses in Unit Operations .....	46
Recommendations for Research.....	51
References .....	57
Appendix A	
Data Table.....	59

# Introduction

## Overview of Chemical Industry Energy Use

Chemicals manufacture is the second largest energy-consuming enterprise in U.S. industry, accounting for over 6.3 quadrillion Btu (quads) of feedstock and process energy use in 2004, or nearly a third of industrial energy use [ACC 2005]. More than half of the energy used by the chemical industry is used as feedstocks (Figure 1). The other half is primarily used to provide heat, cooling, and power to manufacturing processes, with a small amount used for conditioning and lighting buildings.

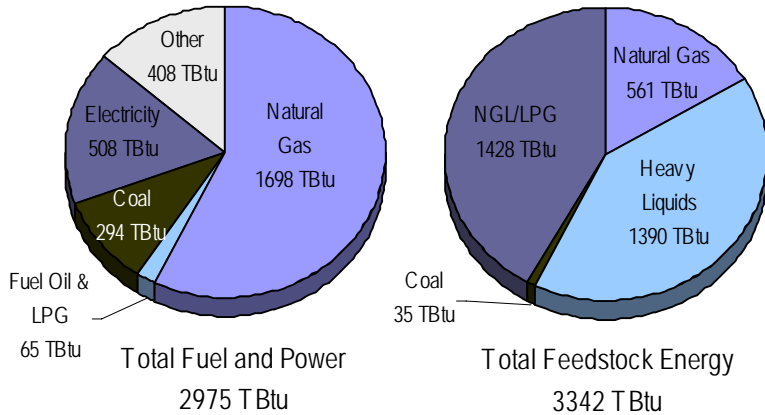


Figure 1. Energy Use in the U.S. Chemical Industry, 2004 [ACC 2005]

The chemical industry has achieved significant energy efficiency gains since the 1970s, precipitated by the Middle East oil crises and resulting pressures on energy supply. Between 1974 and 1986, fuel and power consumed per unit output in the industry decreased by nearly 40% (see Figure 2). But after the easiest energy efficiency improvements were made, the industry energy intensity leveled off. Further improvements in energy efficiency will be necessary for the industry to maintain a competitive edge.

The chemical industry's dependence on energy for raw materials as well as fuel and power makes it particularly vulnerable to fluctuations in energy price. High fuel and feedstock prices can have a profound effect on chemical processing, which typically requires large amounts of energy to convert raw materials into useful chemical products. Recent spikes in natural gas price, for example, caused temporary plant shutdowns of gas-based cracking facilities in some regions of the country. Petroleum and natural gas price increases continue to create price uncertainties in commodity chemical markets, and are a key driver for olefins pricing [CMR 2005].

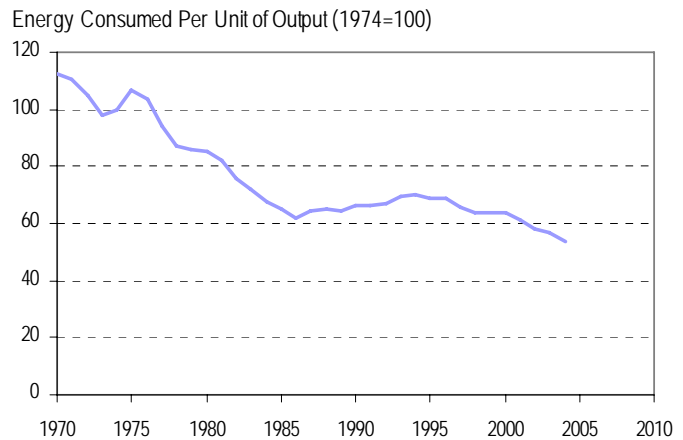


Figure 2. Energy Intensity of the U.S. Chemical Industry [ACC 2003, ACC 2005]

As energy prices continue to rise and supplies become more volatile, chemical companies are increasingly looking toward energy efficiency as a way to reduce production costs and improve their competitive edge. The challenge for today's chemical manufacturers is to effectively focus their resources on improving the equipment and processes that will produce the greatest benefits in energy use, productivity, and yield.

## Objectives of the Analysis

At the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (DOE/EERE), the Industrial Technologies Program (ITP) is supporting research and development to improve the energy efficiency and environmental performance of processes used in many of the basic materials industries. ITP's Chemicals and Allied Processes (CAP) subprogram works specifically with the chemicals, petroleum refining, and forest products industries to accelerate the development of advanced, energy-efficient technologies. Projects are cost-shared by industry and typically involve high-risk, pre-competitive research that individual companies could not fund independently. In many cases, the research has national rather than local benefits, i.e., chemical companies across the nation can potentially reap the energy and economics benefits of research.

To guide research decision-making and ensure that Federal funds are spent effectively, ITP needs to know which manufacturing processes are the most energy-intensive and least efficient. To gain knowledge of process inefficiencies in chemicals manufacture, the ITP CAP program commissioned a "bandwidth" study to analyze the highest energy-consuming chemical processes. The objectives of the study were to

- identify and quantify the inefficiencies of existing technologies and processes in selected chemicals manufacture;
- pinpoint the location of energy losses;
- calculate the recoverable energies for each process;
- examine energy losses in major unit operations that are common across the chemicals selected; and
- Introduce the concept of *exergy* into energy usage and recovery.



A chief advantage of this study is the use of exergy analysis as a tool for pinpointing inefficiencies. Prior analyses have focused only on energy and ignored the quality of energy and the degradation of energy quality. Exergy analysis goes a step further to evaluate the quality of the energy lost, and distinguishes between recoverable and non-recoverable energy. A description of the unique characteristics and benefits of exergy analysis and the results of the study comprise the remainder of this report.



# Methodology

## Energy Bandwidth Analysis

**Energy bandwidth** analysis provides a measure of opportunities for energy savings through improvements in technology, process design, operating practices, or other factors. Bandwidth analysis quantifies the differences between plant process energy consumption levels shown in Figure 3:

1. Current average process energy
2. State of the art process energy
3. Practical minimum process energy
4. Theoretical minimum energy
  - a. Theoretical minimum *process* energy
  - b. Theoretical minimum *reaction* energy

The **current average process energy** (Level 1) is based on the average energy consumption by a typical plant in today's manufacturing environment. A typical plant can reduce its process energy consumption by implementing best practices and incorporating existing state of the art equipment and process technologies and achieve the **state of the art process energy** (Level 2). A plant that has achieved the Level 2 is also referred to as a "World's Best Plant". The **practical minimum process energy** (Level 3) is the industry average process energy requirement for a typical plant after deployment of new process technologies developed through applied research and development (R&D) beyond Level 2. The **theoretical minimum energy** (Level 4) is the absolute minimum process energy required by thermodynamics to convert raw materials into products under ideal conditions. There are two parts of the theoretical minimum energy – the process and the reaction theoretical minimum energies. It is important to note that the practical minimum energy is a "moving target" and its position depends on the level of technology R&D advancements as new ways of improving the frontiers of research are discovered or invented. As the number of R&D breakthroughs increases, the practical minimum process energy will decrease.

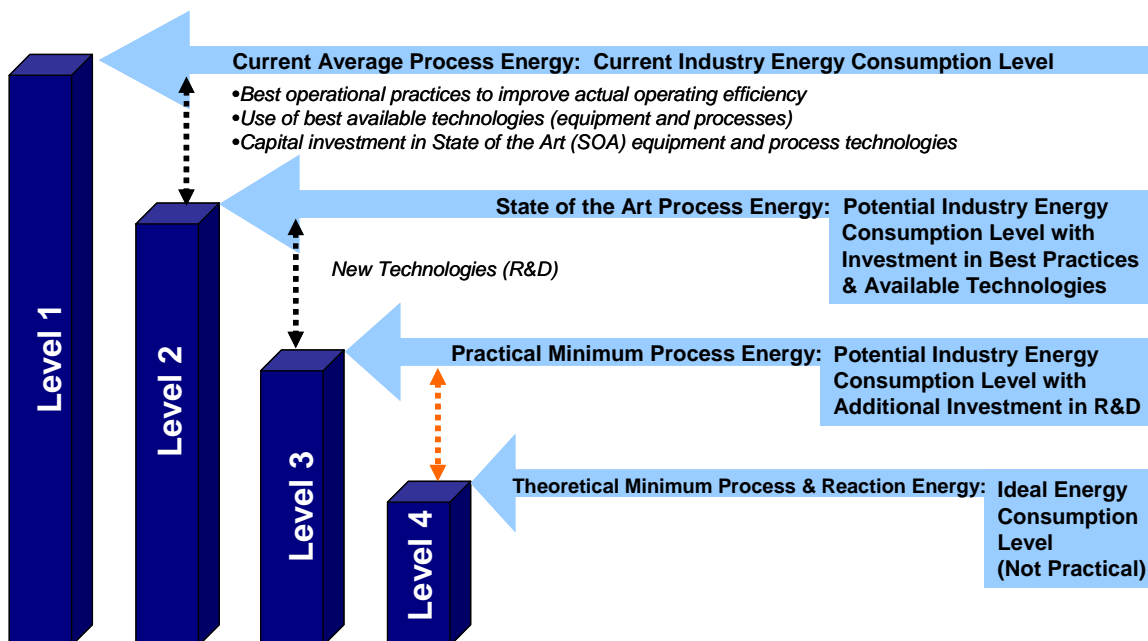
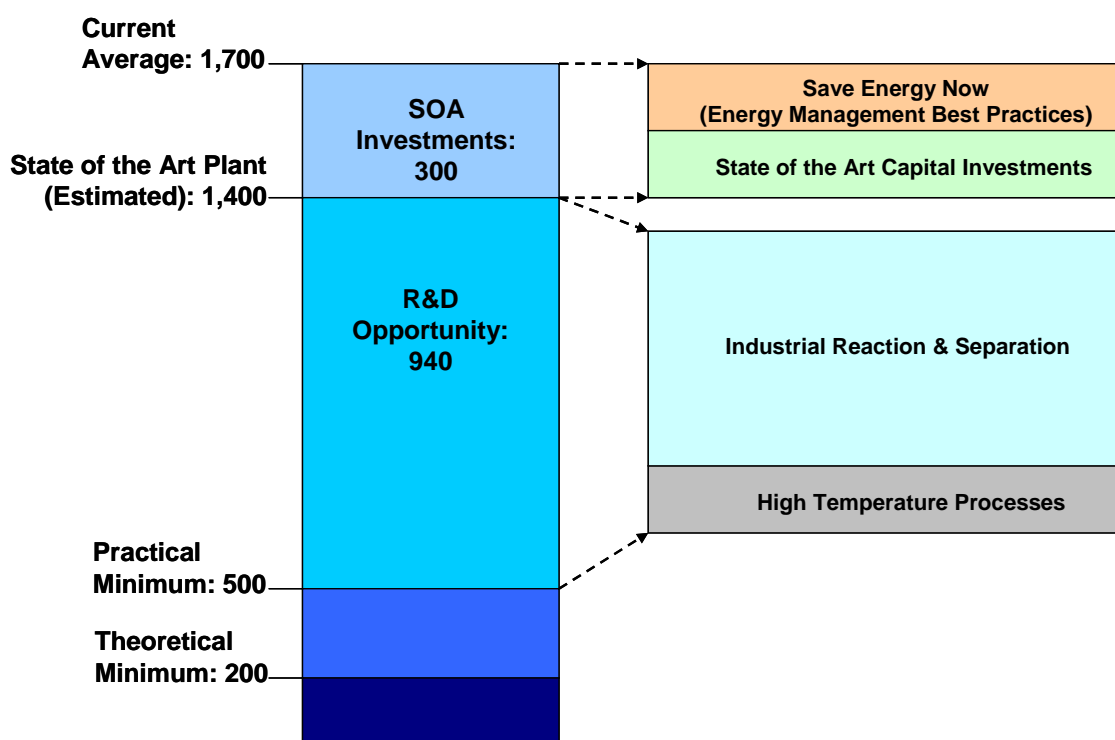


Figure 3. Depiction of Typical Plant Process Energy Consumption Levels and Bandwidths

The differences in these levels represent the opportunities for energy savings, or bandwidths, as shown in Figure 3. For example, the difference between Levels 1 and 2 represents the opportunity to save energy through energy efficiency measures, including best practices such as the Save Energy Now program being implemented by the DOE Industrial Technologies Program, and the adoption of available state of the art equipment and process technologies. This generally corresponds to the external exergy loss or energy recoverable through non-product effluents from a typical plant as defined in the next section. Similarly, the difference between levels 2 and 3 is the opportunity to save energy through deployment of technologies developed through applied R&D. This generally corresponds to internal exergy losses or energy lost through process irreversibilities as defined in the next section.

The energy saving opportunities in the chemical process industry are significant and exergy analysis can assist in pinpointing and quantifying the recoverable energy for each process. Figure 4 presents an estimate of the potential energy savings for the 44 chemical bandwidth products using the four energy levels defined earlier. The energy savings are based on 2004 production volumes [ACC 2005].



**2004 Process Energy Consumption of 44 Chemical Bandwidth Products (Trillion Btu per Year)**

Figure 4. Chemical Bandwidth Analysis Results and Crossover to Industrial Technologies Program

## Introduction to Exergy Analysis

Exergy analysis provides a powerful tool for assessing the quality of energy and quantifying the portion of energy that can be practically recovered. Not all forms of energy are equally valuable for energy recovery. For example, in an energy balance, 1,000 Btu of low pressure steam would compare equally to 1,000 Btu of electricity. In reality, the low-pressure steam has less than a third as much usable energy as the electricity. The steam could be used for heating until its temperature is brought down to the plant environment temperature. At this point the gas still contains energy, but the energy is not useful or available for recovery: it has no exergy.

### Exergy.....

*is defined as the maximum amount of work that can be extracted from a stream as it flows toward equilibrium. This follows the 2<sup>nd</sup> Law of Thermodynamics, which states that not all heat energy can be converted to useful work. The portion that can be converted to useful work is referred to as **exergy**, while the remainder is called **non-exergy input**.*

When applied to a system, such as a manufacturing plant, exergy analysis is used to identify exergy losses and thereby show where useful energy is being wasted. Exergy can be destroyed or lost in two ways. *External* exergy losses are associated with exhaust gasses, cooling water outflow, or other streams leaving the system. These flows contain energy, some portion of which is available for recovery. *Internal* exergy losses are losses that occur within the system every time energy is used in a heat exchanger or other process equipment. In this case no energy leaves the system; energy is conserved but exergy is lost. Internal and external exergy losses can be recovered through a combination of best practices, state-of-the-art technologies, and technologies that are in various stages of R&D.

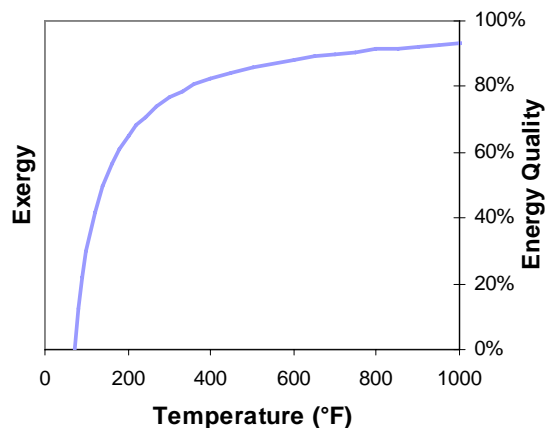


Figure 5. Exergies of a Stream Containing a Fixed Energy Content at Varying Temperature

**External exergy losses** – In industrial processes, most external exergy losses are in cooling water outflows or other effluents. The amount of exergy in a waste stream flow is highly dependent on temperature, as illustrated in Figure 5. A process stream at 110°F has little recoverable energy, but the exergy value increases with temperature. More generally, exergy content depends on the difference between the waste stream and the environment, in terms of temperature, pressure, or chemical composition. A high pressure or highly reactive waste stream would also have higher exergy content.

The ratio of the exergy content to the energy content of an effluent stream is its *quality* (also shown in Figure 5). Although exergy analysis does not account for the economic feasibility of energy recovery, energy quality can be used to gain some

understanding of the potential for recovery. In discussing this analysis, economical energy recovery is considered likely for streams with a quality greater than 20%, possible for some streams with quality 5–20%, and unlikely for streams with a quality below 5%. A significant portion of external exergy losses can typically be recovered through the implementation of best practices (e.g., waste heat recovery), although the percentage of recoverable exergy through best practices will vary by process and depend on the effluent stream quality. The remaining external exergy losses may be recoverable through advanced R&D.

**Internal exergy losses** – Perfectly efficient theoretical processes are reversible, that is, they can proceed in either direction. A perfect, reversible heat exchanger would transfer heat between two streams at equal

temperatures. But heat will not transfer without a temperature difference; real heat exchangers transfer heat from a hotter stream to a colder one. This temperature gradient makes heat transfer irreversible, and the irreversibility results in an exergy loss. No real industrial process is perfectly reversible because it is made up of irreversible processes such as heat transfer, spontaneous chemical reactions, and unrestrained gas expansion. High-temperature processes and those involving highly exothermic reactions are especially prone to large internal exergy losses. To a certain extent, internal exergy losses can be addressed through the development of new technologies, such as advanced catalysts (higher selectivities, conversions per pass) and novel microreactor and separation technologies. Depending on the process, a

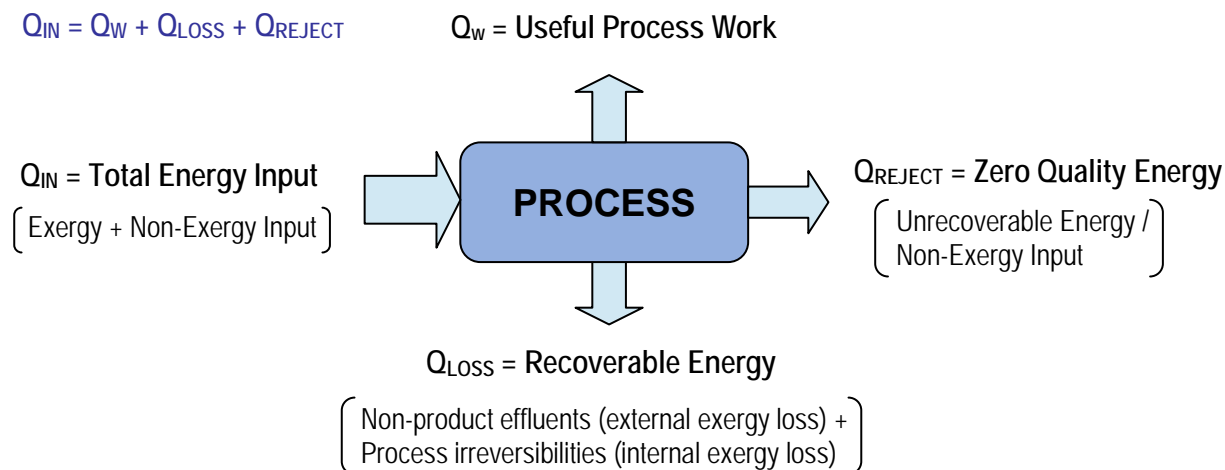


Figure 6. Concept of Exergy in a Chemical Process

portion of internal exergy losses (e.g., throttling) may be recovered through best practices.

The concept of exergy or energy quality is applied to a chemical process in Figure 6. Total energy input ( $Q_{IN}$ ) is comprised of both exergy and non-exergy input. During the process, some of the total exergy input is converted to useful work ( $Q_W$ ), while some is lost due to internal and external energy loss factors ( $Q_{LOSS}$ ). Energy efficiency and energy recovery measures can be used to reduce this loss component. The non-exergy component of total input energy has zero quality and cannot be recovered, but is rejected ( $Q_{REJECT}$ ). Note that Figure 6 represents an endothermic process, in which the chemical reaction requires an energy input. In the case of an exothermic process, the reaction would generate energy, so  $Q_W$  would be negative (or the arrow in Figure 6 would point in the opposite direction).

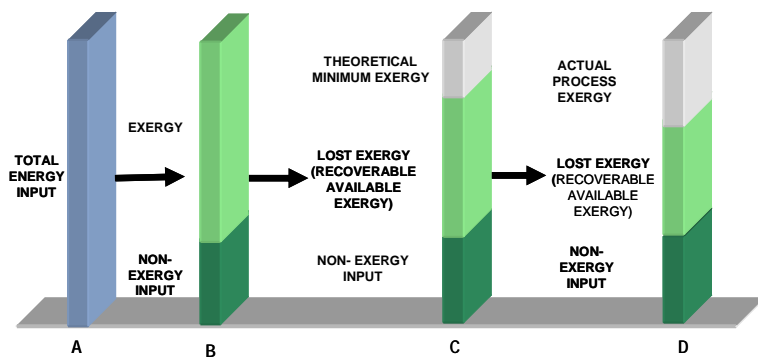


Figure 7. Concept of Exergy, Theoretical Minimum, and Actual Process Energy

Figure 7 shows qualitatively how exergy relates to the energy bandwidth shown in Figure 3. The exergy and non-exergy input shown in bar B represent all the energy inputs. C shows the breakdown of input process energy into theoretical minimum requirements, recoverable energy, and non-exergy components. Bar D illustrates processes that operate with actual process energy requirements; input process energies are higher than the theoretical minimum and recoverable energies are therefore lower.

Again, note that Figure 7 represents a 100% selective, endothermic process, in which the theoretical minimum energy and actual process energy are both positive quantities. Many processes are based on exothermic reactions, which are net energy generators, and therefore have a negative theoretical minimum energy requirement. Other endothermic processes are not 100 % selective, but consume some of the feedstock in exothermic side reactions. In some processes these side reactions generate enough energy to make the actual process energy a negative quantity.

## Selection of Chemical Processes

A large share of energy consumption in the U.S. chemical industry can be attributed to a relatively small number of chemical manufacturing processes and technologies. For this study, many of the most energy-intensive chemicals and related process technologies were selected from a list of the top 80 chemicals, drawn from lists published by the American Chemistry Council [ACC 2005, ACC 2003]. The technologies selected for study are necessary to the manufacture of 44 major chemical products representing about 70% of the production volume of the top 80 chemicals, as shown in Table 1.

The process energy use shown in Table 1 was estimated for each chemical based on current production data (lb) from the American Chemical Council and on total energy input values (Btu/lb) from this analysis. This is a simplified method for deriving the process energy; in several cases the total energy input value computed for one process is applied to the entire production volume, which is actually produced by several different processes (e.g., propylene oxide).

Energy for the manufacture of the 44 chemicals in Table 1 accounts for about 60% of energy consumed by the chemical industry for fuels and power in 2004 [ACC 2005]. Analysis was performed on 53 chemical process technologies associated with the selected chemical products shown in Table 1. The licensors of these technologies and a basic description are provided in Table 2. Two or more competing technologies were selected for seven of the chemicals studied.

Table 1. Chemicals Selected for Analysis		
Chemical	2004 U.S. Production (Billion lb)	Estimated Process Energy (TBtu)
Sulfuric Acid	82.7	10.7
Nitrogen	69.6	11.4
Oxygen	58.3	11.8
Ethylene	56.6	488.6
Propylene	33.8	153.6
Chlorine	26.8	314.7
Ethylene Dichloride	26.7	18.7
Phosphoric Acid	25.3	0.6
Soda Ash	24.3	30.3
Ammonia	23.7	109.1
Vinyl Chloride	16.0 <sup>b</sup>	42.7
Nitric Acid	14.8	3.4
Ammonium Nitrate	13.3	2.3
MTBE	12.8	113.3
Ethylbenzene	12.7	21.1
Urea	12.7	16.2
Carbon Dioxide	12.4	25.8
Styrene	12.1	48.6
Hydrochloric Acid	11.1	0.0
Terephthalic Acid	11.0 <sup>a</sup>	21.1
p-Xylene	9.2	29.5
Formaldehyde	9.1	6.3
Cumene	8.2	8.2
Isobutylene	8.1 <sup>c</sup>	18.6
Ethylene Oxide	8.0	61.9
Methanol	6.5	23.2
Ethylene Glycol	6.4	37.2
Ammonium Sulfate	5.8	4.1
Phenol	5.3	37.0
Butadiene	4.8	6.7
Acetic Acid	4.8	7.7
Propylene Oxide	4.5 <sup>a</sup>	31.3
Carbon Black	3.7	0.0
Acrylonitrile	3.5	15.1
Vinyl Acetate	3.3	9.5
Hydrogen	3.3	1.0
Nitrobenzene	2.8	3.2
Cyclohexane	2.3 <sup>a</sup>	1.1
bisPhenol A	1.9 <sup>a</sup>	4.1
Caprolactam	1.8 <sup>a</sup>	16.7
Aniline	1.8	1.7
Methyl Methacrylate	1.7	6.2
Isopropyl Alcohol	1.6 <sup>a</sup>	6.1
Methyl Chloride	1.3	0.5
<b>TOTAL (44 Chemicals)</b>	<b>666.0</b>	<b>1780.9</b>
<b>TOTAL (Top 80 Chemicals)<sup>a</sup></b>	<b>948.5</b>	<b>---</b>

<sup>a</sup> 2002 data

<sup>b</sup> Equal to PVC production volume

<sup>c</sup> Volume estimated as a fraction of MTBE

Table 2. Chemical Technologies Selected for Analysis

Chemical	Process Technologies Analyzed
Sulfuric Acid	Oxidation of molten sulfur to sulfur dioxide and further oxidation by Contact process to sulfur trioxide, which is absorbed in water
Nitrogen	<i>Union Carbide</i> – High purity nitrogen by cryogenic rectification of air
Oxygen	<i>Union Carbide</i> – Ultra-high purity oxygen by cryogenic rectification of air
Ethylene	<i>Braun</i> – Conventional cracking of propane with front-end de-ethanization <i>M.W. Kellogg</i> – Millisecond cracking of naphtha with front-end de-methanization Steam cracking of ethane in a pyrolysis furnace
Propylene	<i>Fina Research</i> – Production from hydrotreated cracked naphtha using a de-aluminated silicalite catalyst (ZSM-5) with a silica binder
Chlorine	Electrolysis of sodium chloride in a diaphragm cell, producing chlorine and caustic soda
Ethylene Dichloride	Oxychlorination of ethylene by hydrogen chloride in a fluidized bed using air
Phosphoric Acid	Extraction of phosphorus pentoxide from phosphate rock and conversion to aqueous acid
Soda Ash	<i>Asahi Glass/ICI</i> – Modified Solvay process: reaction of ammonia, carbon dioxide, and sodium chloride
Ammonia	Derived from Szargut and Cremer (see references) – Reforming of methane
Vinyl Chloride	<i>Hoechst</i> – Gas-phase de-hydrochlorination of ethylene dichloride
Nitric Acid	Derived from Szargut (see references) – Oxidation of ammonia with air on a platinum/rhodium alloy catalyst
Ammonium Nitrate	<i>Stamicarbon</i> – Nitration of ammonia in a liquid-phase loop reactor, catalyzed by sulfuric acid
MTBE	Derived from Al-Jarallah, et al. (see references) – Reaction of methanol and isobutylene using a sulfuric acid catalyst
Ethylbenzene	<i>Lummus Crest/Unocal/UOP</i> – Liquid-phase alkylation of benzene <i>Mobil/Badger</i> – Vapor-phase alkylation of benzene/ethylene
Urea	<i>Mitsui</i> – Reaction of ammonia and carbon dioxide in a tower reactor to form ammonia carbamate, which is partially dehydrated to urea
Carbon Dioxide	<i>DOW</i> – Absorption from gas power plant flue gas (sulfur-free) with mono-ethanolamine
Styrene	<i>Lummus Crest</i> – Zeolite-based liquid-phase dehydrogenation of ethylbenzene <i>Fina/Badger</i> – Vapor-phase dehydrogenation of ethylbenzene
Hydrochloric Acid	Reaction of hydrogen and chlorine in a burner-reactor
Terephthalic Acid	<i>Amoco</i> – Liquid-phase oxidation of p-xylene with cobalt-manganese-bromine catalyst
p-Xylene	Production from a mixture of C <sub>8</sub> aromatic isomers (p-xylene, o-xylene, m-xylene, ethylbenzene) via front-end isomerization and fractionation (generic)
Formaldehyde	<i>BASF</i> – Production from methanol using a silver catalyst
Cumene	<i>UOP</i> – Solid phosphoric acid (SPA)-catalyzed reaction of benzene/propylene feed Zeolite-catalyzed – Propylene alkylation of benzene using zeolite catalyst (similar to Mobil/Badger, UOP and DOW-Kellogg zeolite processes) AlCl <sub>3</sub> -catalyzed – Propylene alkylation of benzene using AlCl <sub>3</sub> catalyst (similar to Monsanto-Kellogg zeolite process)
Isobutylene	Catalytic dehydration of t-butyl alcohol
Ethylene Oxide	<i>Shell/Union Carbide</i> – Direct oxidation of ethylene with oxygen
Methanol	<i>ICI LP</i> – Production from natural gas using low-pressure reforming with a nickel-based catalyst in the reformer and a copper catalyst for methanol synthesis <i>Lurgi</i> – Two-stage combined reforming process
Ethylene Glycol	Thermal hydrolysis of ethylene oxide
Ammonium Sulfate	Reaction of ammonia, carbon dioxide, and waste gypsum

Table 2. Chemical Technologies Selected for Analysis	
Chemical	Process Technologies Analyzed
Phenol	Peroxidation of cumene to cumene hydroperoxide, followed by cleavage into phenol and acetone Oxidation of toluene to benzoic acid, followed by conversion to phenol without co-products
Butadiene	<i>Nippon Zeon</i> – Recovery as by-product from steam cracking of liquid feedstocks (C <sub>5</sub> s, C <sub>6</sub> s, C <sub>7</sub> s, C <sub>8</sub> s)
Acetic Acid	<i>Chiyoda/UOP</i> – Low-pressure methanol carbonylation using a rhodium catalyst and methyl iodide as a promoter
Propylene Oxide	<i>Arco/Halcon</i> – Production with co-product t-butyl alcohol from isobutane and propylene
Carbon Black	Partial oxidation of oil with air in a furnace
Acrylonitrile	<i>SOHIO/BP</i> – Ammoxidation of propylene using a bismuth molybdate-based catalyst <i>SOHIO/BP</i> – Ammoxidation of propane in a fluidized bed reactor using a metal catalyst complex of vanadium, tin, and tungsten
Vinyl Acetate	<i>BP</i> – Vapor-phase acetoxylation of ethylene
Hydrogen	Steam reforming of natural gas
Nitrobenzene	<i>American Cyanamid</i> – Liquid-phase reaction of nitric acid with benzene
Cyclohexane	<i>Toray</i> – Vapor-phase catalytic hydrogenation of benzene with a nickel catalyst
bisPhenol A	Liquid-phase reaction of phenol and acetone, catalyzed by hydrochloric acid
Caprolactam	Beckmann rearrangement of cyclohexanone oxime
Aniline	Vapor-phase catalytic reduction of nitrobenzene
Methyl Methacrylate	Reaction of acetone with hydrogen cyanide, followed by rearrangement to methacrylamide sulfate, which is cracked to produce methyl methacrylate and ammonium bisulfate
Isopropyl Alcohol	<i>Deutsche Texaco</i> – Hydration of propylene over a cation exchange resin catalyst
Methyl Chloride	Liquid-phase chlorination of methanol



## Energy and Exergy Modeling Methodology

### *Model Integration*

To calculate recoverable energy, energy and exergy analysis were applied to the selected chemical processes using three tools:

- AspenPlus, steady-state process modeling software from AspenTech that was used to develop process models and solve for stream properties;
- ExerCom, an exergy calculator developed by Jacobs Engineering, Inc., of the Netherlands, that interfaces with Aspen Plus and determines exergy for individual process streams; and
- a computer program developed by Psage Research that interfaces with the AspenPlus and ExerCom models and calculates energy and exergy balances around each unit operation.

A schematic of the modeling approach is shown in Figure 8. The analysis begins with flowsheet models of the processes, drawn from several sources. Where available, process models were taken from the SRI Consulting/Aspen Process Economics Program (PEP) library. This library uses public information and in-house engineering to reproduce the technology of licensors, plant operators, or research organizations. Other process models were developed from SRI flowsheets, and a few from open literature sources. The AspenPlus simulation uses the flowsheet models to obtain process energy and material balances for each chemical manufacturing process.

The ExerCom model uses the output of the AspenPlus simulation, along with internal databases of standard chemical exergies and enthalpies, to compute the exergy and energy of all of the liquid and gaseous material streams. ExerCom's internal databases contain thermodynamic data for a limited number of chemical species, requiring extra calculations for those that are missing. The exergies of heat, work, and solid streams must also be calculated manually.

In the last phase of modeling, the Psage-developed program interfaces directly with the AspenPlus and ExerCom results to calculate exergies of heat, work, and solid streams around individual process units and the overall process model. Exergies of heat streams not calculated by ExerCom are computed from enthalpies using the Carnot quality factor ( $\eta_c$ ). Exergy inflows not included within the model boundaries (mainly refrigeration and separation units) are estimated based on exergetic efficiencies of similar units.

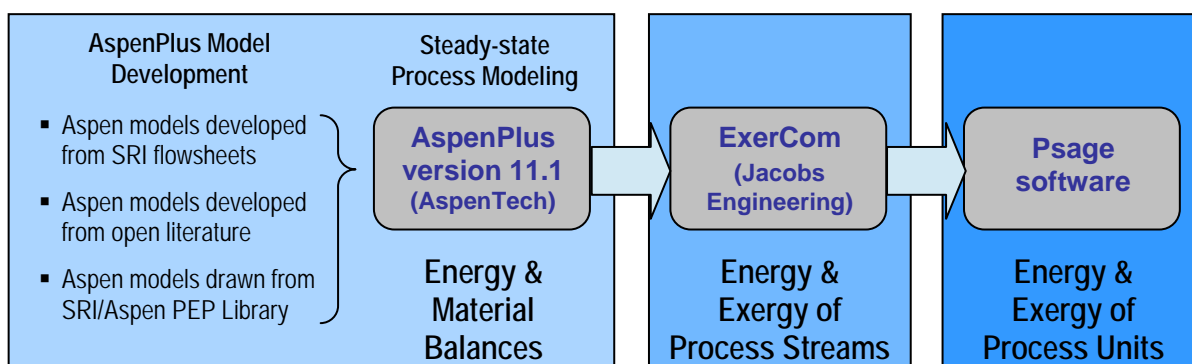


Figure 8. Integrated Modeling Approach Used for Exergy and Energy Analysis

## Unit Processes and Equipment

A number of assumptions were necessary to calculate the energy and exergy losses of specific equipment included in each process flowsheet. The process units modeled in the analysis are shown in Table 3, along with the basic assumptions made for determining energy and exergy losses. Examining the energy and exergy losses calculated for specific unit operations helps to pinpoint the types of processing units that should be targeted for future efficiency improvement or technology development.

Process Unit	Description
Reactors (exothermic)	In exothermic reactors, the heat of reaction is removed by some combination of sensible heat, streams leaving the reactor, or steam generated and used elsewhere in the plant (ordinarily no external exergy loss). Internal exergy losses can be substantial (generally irreversibilities created by mixing of streams of very different temperature and composition and by heat transfer across large temperature differences).
Reactors (endothermic)	In endothermic reactors, feed streams supply all of the energy absorbed in the reaction. Internal exergy losses are considerable because feed streams are much hotter than reactor effluents.
Distillation Columns	Distillation columns separate chemicals by boiling point differences. The energy and exergy of each stream, reboiler, and condenser are calculated. External exergy losses suggest the extent to which energy recovery is possible. Internal exergy losses are created by process irreversibilities arising from large driving forces of temperature and composition differences.
Heat Exchangers	Two heat exchanger configurations are possible: (1) process streams on both sides, or (2) process stream on one side and heating or cooling medium on the other. For (1), exchangers have no external exergy loss, and internal exergy losses due to irreversibilities depend on the temperature difference between heated and cooled media. For (2), external exergy loss determines the quality of the energy loss. A low exergy loss, for example, would suggest little opportunity for energy recovery.
Process Furnaces	A variety of furnaces are used to superheat steam, heat process streams, or enable chemical reactions (reformers). When the fuel is not included as a stream, energy or external exergy losses due to fuel combustion and stack gasses are not included in the analysis. Large internal exergy losses are typical, due to large changes in process stream temperatures and large driving forces for heat transfer.
Compressors & Expanders	In compressors and expanders, energy and external exergy losses result from intercoolers and process irreversibilities. Internal exergy losses depend on the difference in temperature and pressure between inlet and outlet gas streams and on the assumed pump or compressor efficiency.
Pumps	Not all pumps are included in the flowsheets. When they are indicated, they do not contribute significantly to exergy or energy losses.
Drums/Tanks	Drums and tanks have no heaters or coolers, and hence no energy or external exergy losses. In flash drums, internal exergy losses are due to changes in pressure, state, and composition between inlet and outlet streams. Receivers with multiple inlets and one outlet stream have internal exergy losses due to changes in stream temperature and composition. Knockout drums and other units have modest internal exergy changes.
Mixers/Splitters	Mixers and splitters are essentially artifacts of the model (simulating mixing or splitting of streams) and do not contribute significantly to the exergy analysis. Internal exergy losses indicate the extent of process irreversibilities.
Other Equipment	Other equipment includes pressure swing absorption units, multi-effect evaporators, and other separators. Some are modeled as black box units, and not all have energy or exergy losses.

## Model Output

The integrated modeling approach produces a number of energy and exergy quantities for each chemical process and individual unit operation (see Table 4). These quantities provide a process efficiency baseline against which new or improved technologies can be compared. A key output is the potentially recoverable energy ( $Q_{LOSS}$ ), which can be used to establish potential for improved efficiency.

Table 4. Model Outputs
<b>Total Process Energy Input (<math>Q_{IN}</math>)</b> – all energy inputs to the process regardless of quality
<b>Total Process Exergy input (TPEI)</b> – the component of input energy that can be converted to work or recovered
<b>Actual Process Exergy (<math>Q_W</math>)</b> – the component of input exergy that is converted to useful work
<b>Theoretical Minimum Process Energy (TMPE)</b> – the minimum amount of energy required for the process based on chemical reactions and ideal or standard conditions and 100% yield
<b>External Exergy Loss (EEL)</b> – potentially recoverable energy in the form of non-product effluents, such as by-products, cooling air, and wastewater
<b>Internal Exergy Loss (IEL)</b> – potentially recoverable energy lost through process irreversibilities
<b>Potentially Recoverable Available Energy (<math>Q_{LOSS}</math>)</b> – the sum of recoverable energies (IEL and EEL)

A sample output of the analysis is provided in Figure 9 for the process model based on production of vinyl chloride monomer (VCM) from ethylene dichloride. The analysis illustrates that a portion (about 8%) of the energy input to this endothermic process is available downstream as recoverable energy.

Analysis of the performance of individual unit operations within each process helps to pinpoint the locations of energy and exergy losses in each of the processes. For production of vinyl chloride monomer, for example, the analysis revealed that the largest energy and exergy losses were due to vaporization of ethylene dichloride, the endothermic furnace reactor (rapid quench), low temperature distillations, and separation of hydrochloric acid (HCl).

Chemical reactions are either endothermic (heat absorbing) or exothermic (heat generating). The endothermic reaction in Figure 9 has a positive value for energy converted to useful work ( $Q_W$ ), indicating that energy is absorbed by the process. In exothermic reactions, additional heat energy is generated by the process and  $Q_W$  has a negative value.

The modeling outputs for each of the chemical technologies selected can be evaluated to identify sources of inefficiency and potential improvement targets. Energy and exergy losses, for example, can be sorted and ranked across all the chemical technologies by the same common unit operations to reveal energy efficiency trends and provide further focus for targeting research.

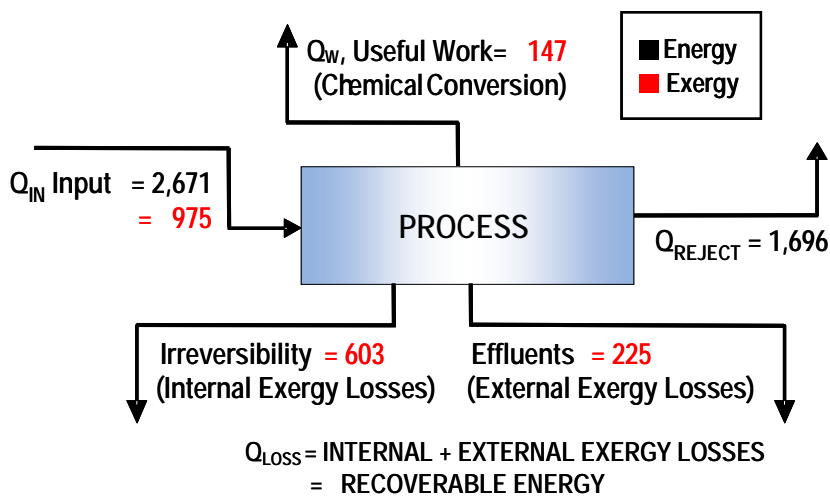


Figure 9. Sample Output of Energy and Exergy Analysis for Vinyl Chloride Monomer (Values in Btu/lb of VCM)

## Limitations of the Approach

The results of the study provide an overall view of process energy and exergy use and loss trends. However, the results are based on models rather than actual plant data. SRI Consulting utilizes public information and in-house engineering expertise to develop the AspenPlus models that serve as the basis for the energy and exergy analysis. While the SRI AspenPlus models can approximate the process inputs, outputs, and design, the results may not reflect actual plant performance because:

- kinetic data and proprietary process data are not always available;
- available thermodynamic data are of limited accuracy, and thermodynamic models are limited in ability to predict stream properties;
- complex process steps may be simplified in the model;
- many companies have optimized their plants beyond what is reported in the public domain; and
- SRI Aspen model results are composed of a specific mix of technologies and equipment, and may not apply where a different mix of technologies and equipment is used.

In addition, results do not reflect external factors that may influence plant performance. For example, large capital assets that could be improved may not be replaced until they reach the end of their useful life, regardless of the potential benefits. Environmental regulations or other factors (permitting, site limitations) may also have an impact on the feasibility of reducing energy and exergy losses.

While potentially recoverable energy does provide a good perspective on efficiency opportunities, the analysis does not provide insight on the true economic feasibility of recovering energy. For example, economic factors such as limited funds for plant upgrades, poor markets, corporate investment philosophy, and the high cost of environmental compliance could all have an impact on economic feasibility. Although the study does not account for economic factors, recoverable energy is measured by the quality factor, which inherently includes the consideration that low quality energy is probably not economically suitable for recovery.

Despite the potential for discrepancies between the study results and actual plant performance, this analysis remains a powerful tool for pinpointing targets for improvement, provided the limitations are kept in mind.

# Summary of Results

## Overview of Results

Energy and exergy data like that shown in Figure 9 were developed for all 53 of the process technologies studied, including multiple technologies for some products. A summary of the results are shown in Table 5. Further results, including internal and external exergy losses, are given in Appendix A.

There is great potential for energy recovery in the chemical processes analyzed. The total potentially recoverable energy identified for the 53 processes studied is nearly 1,500 trillion Btu (dividing production between multiple technologies when applicable, as indicated below in Table 5). As defined earlier, this recoverable energy is a sum of internal and external exergy losses, and does not address the economic feasibility of recovery.

Process	Energy Input (Q <sub>IN</sub> )	Exergy Input	Process Exergy (Q <sub>w</sub> )	Theoretical Minimum Energy	Recoverable Energy (Q <sub>LOSS</sub> )	Ratio of Q <sub>LOSS</sub> /Q <sub>IN</sub> *	Recoverable Energy (TBtu/yr)**
Chlorine	11,730	11,032	3,970	3,086	7,062	60%	189.5
Sulfuric Acid	129	81	-1,506	-2,900	1,588	1231%	131.4
Hydrogen	291	283	-33,033	7,391	33,317	11449%	109.7
Ethylene (from naphtha)	8,139	5,035	217	-989	4,818	59%	109.0
Ethylene Oxide	7,741	5,735	-6,720	734	12,456	161%	99.6
Ammonia	4,596	3,543	-351	414	3,894	85%	92.4
Ethylene (from ethane)	9,125	6,411	2,998	1,538	3,413	37%	77.2
Propylene	4,548	3,560	1,440	846	2,119	47%	71.6
Terephthalic Acid	1,919	1,157	-4,730	3,047	5,887	307%	64.7
Ethylene (from propane)	8,656	5,534	326	650	5,208	60%	58.9
Carbon Black	0	0	-12,566	-803	12,567		46.6
MTBE	8,868	2,572	-135	124	2,706	31%	34.6
Acrylonitrile (from propylene)	4,364	1,020	-8,015	4,355	9,035	207%	31.3
Ethylene Dichloride	701	168	-971	-784	1,139	162%	30.4
Formaldehyde	698	115	-3,209	802	3,324	476%	30.1
Phenol (from cumene)	6,942	2,016	-2,611	-1,470	4,627	67%	24.6
Nitric Acid	232	207	-1,401	1,953	1,609	694%	23.8
Propylene Oxide	7,001	1,839	-2,686	1,156	4,525	65%	20.2
Soda Ash	1,250	425	-327	-1,754	754	60%	18.3
Methanol (ICI)	4,883	871	-4,546	802	5,417	111%	17.5
p-Xylene	3,228	1,702	-133	5	1,835	57%	16.8
Methanol (Lurgi)	2,273	849	-4,125	526	4,974	219%	16.1
Ethylene Glycol	5,853	1,977	-143	-415	2,120	36%	13.5
Vinyl Chloride	2,671	975	147	142	828	31%	13.2
Methyl Methacrylate	3,599	742	-6,067	-6,359	6,809	189%	11.7
Carbon Dioxide	2,083	508	-426	N/A	935	45%	11.6
Styrene (Fina/Badger)	3,365	1,122	-369	340	1,491	44%	9.0
Ethylbenzene (Lummus)	1,528	1,131	-231	273	1,363	89%	8.7

Table 5. Energy and Exergy Analysis Results (Btu/lb)							
Process	Energy Input (Q <sub>IN</sub> )	Exergy Input	Process Exergy (Q <sub>w</sub> )	Theoretical Minimum Energy	Recoverable Energy (Q <sub>LOSS</sub> )	Ratio of Q <sub>LOSS</sub> /Q <sub>IN</sub> *	Recoverable Energy (TBtu/yr)**
Styrene (Lummus)	4,703	1,697	305	340	1,392	30%	8.4
Ethylbenzene (Mobil/Badger)	1,787	965	-317	273	1,282	72%	8.2
Oxygen	202	202	67	N/A	135	67%	7.9
Urea	1,276	503	-63	-289	566	44%	7.2
Nitrogen	164	164	63	N/A	102	62%	7.1
Phosphoric Acid	22	10	-270	-394	279	1268%	7.1
Ammonium Nitrate	171	23	-499	-502	522	305%	6.9
Vinyl Acetate	2,866	891	-1,194	-1,060	2,084	73%	6.9
Caprolactam	9,521	2,304	-1,318	-170	3,622	38%	6.3
Acetic Acid	1,612	786	-512	436	1,297	80%	6.2
Hydrochloric Acid	0	0	-530	-1,124	530		5.9
Isobutylene	2,288	518	53	54	465	20%	3.8
Aniline	956	368	-1,548	-2,093	1,915	200%	3.4
Nitrobenzene	1,147	419	-503	421	922	80%	2.6
Ammonium Sulfate	709	249	-148	-701	397	56%	2.3
Butadiene	1,382	468	55	N/A	413	30%	2.0
Cumene (AlCl <sub>3</sub> )	1,124	440	-240	526	680	60%	1.9
bisPhenol A	2,131	649	-290	-491	938	44%	1.8
Cyclohexane	465	229	-543	-499	772	166%	1.8
Cumene (Zeolite)	1,061	375	-248	526	623	59%	1.7
Cumene (SPA)	812	328	-245	526	574	71%	1.6
Isopropyl Alcohol	3,880	808	-124	-50	932	24%	1.5
Methyl Chloride	398	249	-455	-250	703	177%	0.9
Phenol (from toluene)	4,787	2,149	-12,860	-3,556	15,009	314%	0.0
Acrylonitrile (from propane)	5,381	1,392	-13,152	5,509	14,544	270%	0.0

- Negative values indicate an exothermic reaction, net chemical conversion exergy inflow

N/A A separation process without chemical reaction

\* Ratios may be higher than 100% because the input energy does not include heat generated by exothermic reactions

\*\* Where multiple processes are modeled for a single product, production is assumed to be evenly divided among the technologies, except for phenol and acrylonitrile, where only one of the technologies is commercial. For ethylene, production is assigned 40%, 40%, and 20% to naphtha, ethane, and propane technologies, as discussed in the chemical profile.

A comparison of the recovery energy potential for each chemical product is shown in Figure 10, in descending order. Where multiple technologies were evaluated, the sum accounts for the approximate prevalence of the competing technologies. Ethylene, chlorine, sulfuric acid, hydrogen, ethylene oxide, and ammonia exhibit the largest potentials for energy recovery.

Many of the energy losses are associated with waste emissions such as cooling water, air, and purge streams, and by-product streams. However, exergy analyses have revealed that such streams may not always contain sufficient recoverable energy to justify energy recovery strategies. Exergy losses associated with waste recovery boilers and throttling can also be significant. Irreversibilities (or internal exergy losses) in the technologies studied were prevalent in furnaces, high temperature reactors, cooling of high temperature reactor effluents, refrigeration, and refrigerated separations.

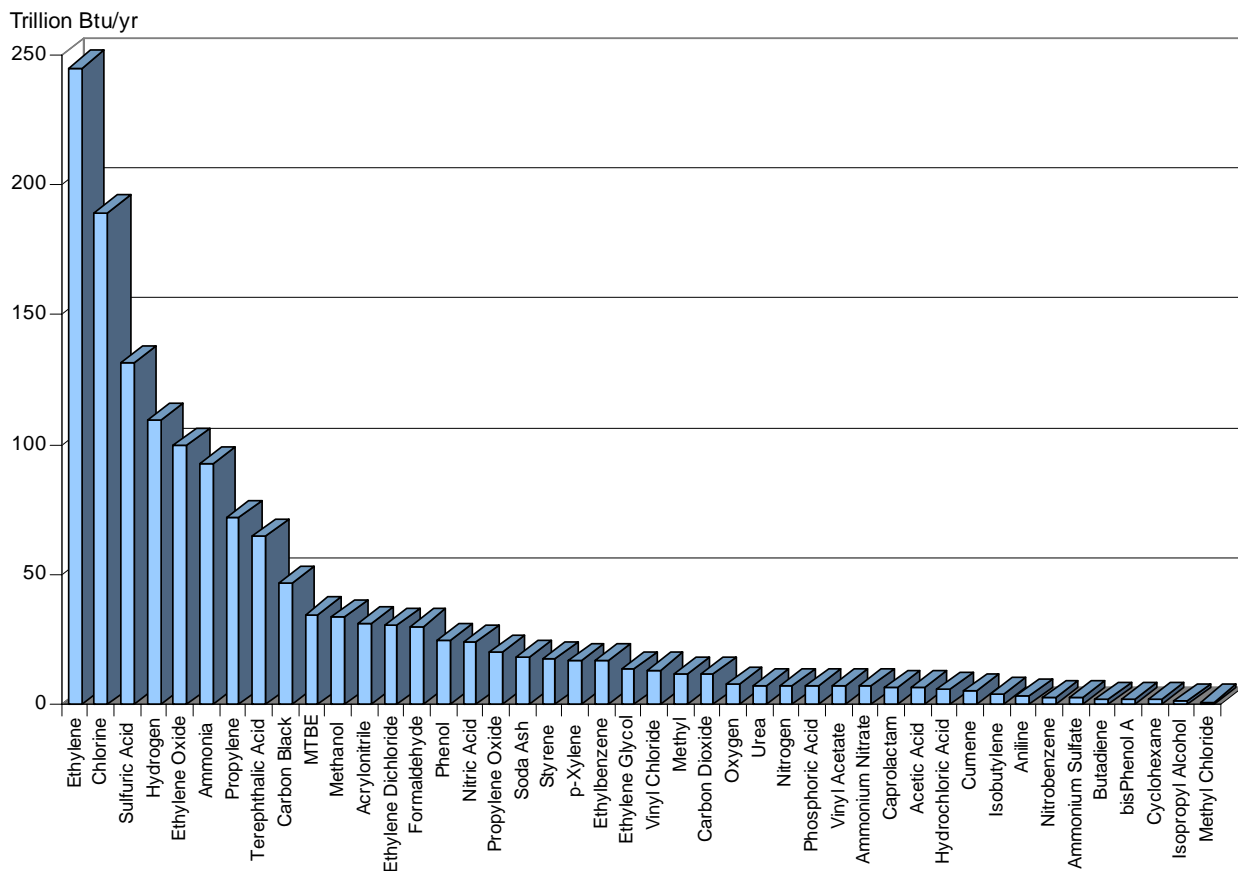


Figure 10. Comparison of Recoverable Energy Across Chemical Technologies

## Trends Observed in the Bandwidth Analysis Results

The data in Table 5 is presented graphically in Figures 11, 12, 13, and 14 to demonstrate the differences between using energy and exergy analyses to identify and prioritize industrial energy saving opportunities. R&D programs commonly focus funds and personnel on areas with the greatest potential for reducing energy use such as the most energy-intensive processes or technologies, which are determined based on the total energy input. However, in this approach, low and high quality energy inputs are considered equally. As this analysis demonstrates, energy quality can be an important factor when considering which process technologies to pursue for the greatest energy savings potential. Figures 11 and 12 show the top ten bandwidth chemicals by total energy and exergy input, respectively, and it is seen that in the case of ethylene glycol and phenol, a significant portion of the total energy input is low quality energy. When energy quality is considered in the exergy analysis, these chemicals are replaced by p-xylene and terephthalic acid which have higher exergy inputs and offer the potential for greater energy recovery. This poses the question of whether energy or exergy analysis should be used to determine opportunities for energy savings.

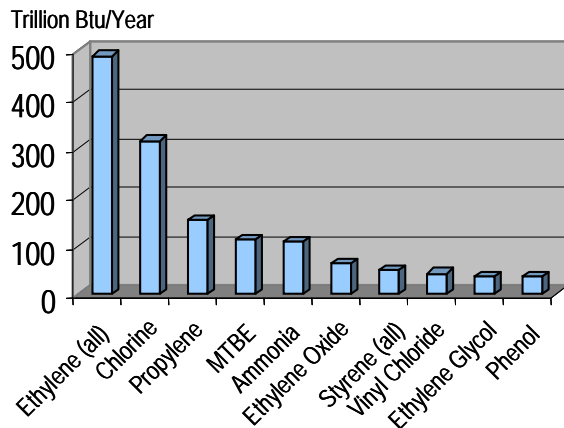


Figure 11. Top 10 Chemical Bandwidth Products by Total Energy Input

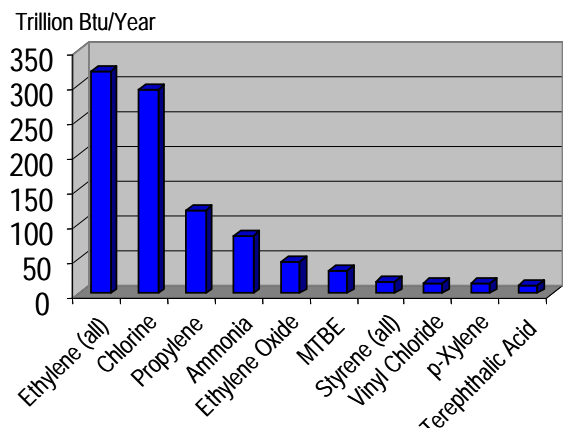


Figure 12. Top 10 Chemical Bandwidth Products by Total Exergy Input

Once the high priority products/processes have been identified, it is useful to look at the total recoverable energy (based on  $Q_{Loss}$ ) which is composed of the internal and external exergy losses. These correspond to the energy that can be recovered through the implementation of best practices and state of the art technologies, and new technologies developed through advanced R&D. As Figures 13 and 14 demonstrate, the energy saving opportunities for advanced R&D are significantly greater than the those for best practices and state of the art technologies. The composition of the top ten chemical products ranked by internal and external exergy losses also differs, indicating that the process technologies that the Federal government programs should focus their efforts on will depend on the mission of the program. Education, training, and outreach may be central to reducing external exergy losses while the reduction of internal exergy losses will depend on basic and applied R&D. These results do not diminish the importance of encouraging existing plants to attain the state of the art plant status; rather, they highlight that both best practices/state of the art technologies and advanced R&D will be necessary to help the chemical process industry minimize its energy consumption.

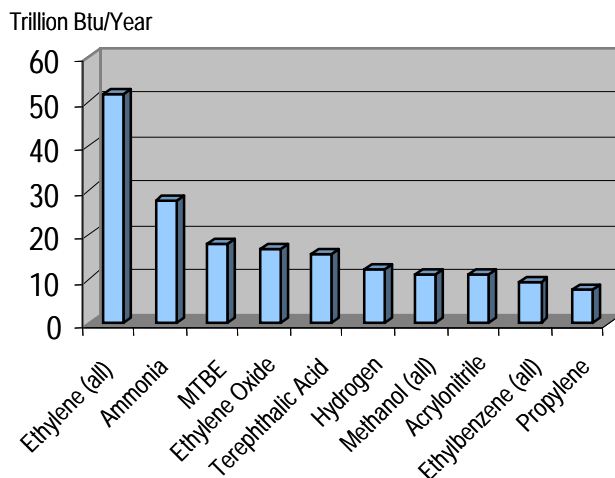


Figure 13. Top 10 Chemical Bandwidth Products by Total External Exergy Losses

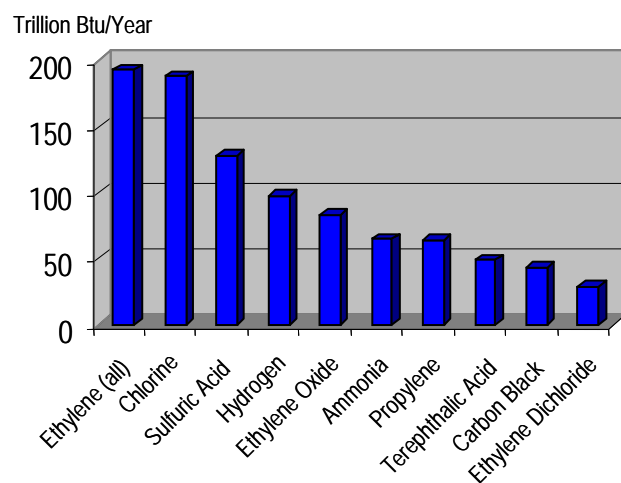


Figure 14. Top 10 Chemical Bandwidth Products by Total Internal Exergy Losses



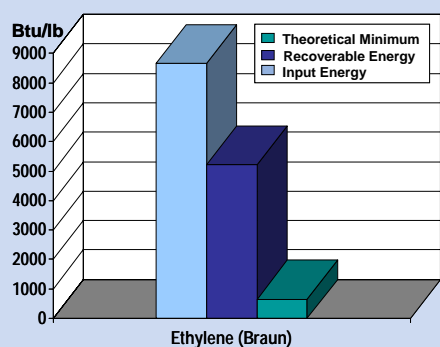
## Chemical Bandwidth Profiles

A brief summary and analysis of the results obtained for each chemical product are provided to give perspective on the assumptions used and the unique aspects of each technology. Insights are given on the largest sources of energy consumption as well as process inefficiencies. Summaries are provided in rank order of descending potential energy recovery (corresponding with Table 5). In addition, the key differences between multiple technologies are analyzed. This is an important benefit of the combined energy and exergy modeling approach – different technologies used to produce the same chemical product can be compared in terms of unit operations and potential for energy and exergy recoveries.

Each profile describes the major sources of energy and exergy losses and makes a comparison of the total process energy inputs to theoretical minimum energy requirements. Energy losses provide an overall picture of process inefficiencies; external and internal exergy losses give a better indication of energy that may be recoverable, and are based on energy quality, as discussed earlier. A low ratio of external exergy loss to total energy loss (low energy quality) indicates energy recovery may not be very feasible. High internal exergy losses indicate substantial process irreversibilities that may be difficult or technically impossible to mitigate.

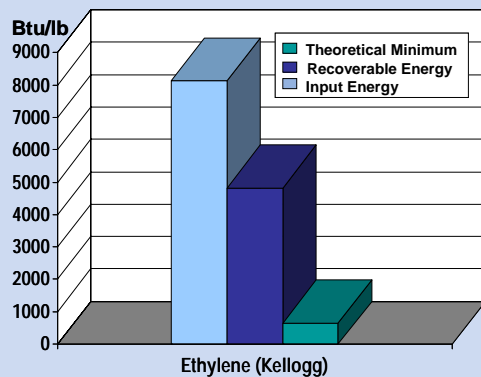
## Ethylene

**Cracking of Propane (Braun)** – This process uses light hydrocarbons such as propane or ethane derived from natural gas liquids as a feedstock. However, with the rise in natural gas prices, most new ethylene capacity is being based on cheaper naphtha or gas oil feeds. Total process energy required is about 13 times greater than the theoretical minimum. The greatest sources of energy-exergy losses include high temperature cracking, quenching of cracked products, and complex low-temperature separations of products and co-products. Heat exchangers (process exchangers, interstage coolers, quenching exchangers) and distillation columns (e.g., C2 splitter) comprise the majority of high energy-consuming equipment. Losses arise primarily from differing temperatures, compositions, and pressures of various streams. Virtually all exergy losses in cracking and quenching are due to the quenching exchangers, which sequentially quench the reaction product gas. The C2 splitter contributes to exergy losses in product separation. About 40% of energy is lost to gas refrigerated cooling, and another 27% is lost to cooling water during interstage gas compressor cooling. The quality of recoverable energy is high enough to generate high-medium pressure steam.



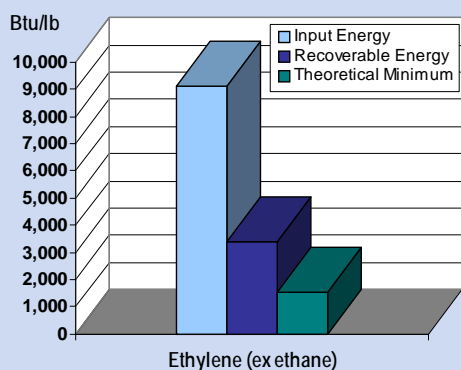
Ethylene from Propane (Braun) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Cracking And Quenching	425	6	38	1046	1084	21
Compression And Deacidification	1879	27	208	590	798	15
Deethanization	1294	18	231	65	296	6
Demethanization	1402	20	554	1106	1660	32
Product Separation	1296	18	255	306	561	11
Heat & Refrigeration Recovery	761	11	520	287	808	16
<b>TOTALS</b>	<b>7055</b>		<b>1806</b>	<b>3402</b>	<b>5208</b>	

**Cracking of Naphtha (Kellogg)** – This process is based on naphtha or gas oil, the feedstock chosen for most new plants in the U.S. today. As opposed to the propane process, the highest energy-exergy consumption is concentrated in the front end of the process. This naphtha process is more exothermic, requiring less input energy, but has double the exergy losses in cracking and quenching due to a higher compression ratio (525 psia versus 140 psia for the propane process). The total process energy required is about 12 times greater than the theoretical minimum. Substantial losses occur in the demethanizer column due to the condenser, which uses ethylene refrigerant as coolant. Large temperature differences create significant exergy losses in the cracking furnaces and large towers of the cracking and quenching section. The cracked gas compressor interstage coolers are also large sources of losses.



Ethylene from Naphtha/Gas Oil (Kellogg) Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Cracking And Quenching	1851	24	183	1678	1861	39
Compression And Deacidification	2958	38	208	540	748	16
Demethanization	1712	22	614	359	974	20
Deethanization	335	4	60	336	396	8
Product Separation	109	1	17	184	201	4
Heat and Refrig. Recovery	842	11	84	554	638	13
<b>TOTALS</b>	<b>7807</b>		<b>1167</b>	<b>3651</b>	<b>4818</b>	

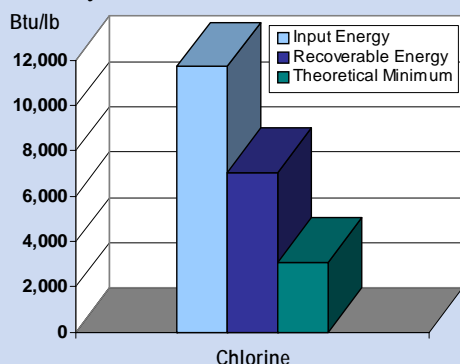
**Ethane Pyrolysis** – This process is based on steam cracking of ethane, which is derived from natural gas. Much of U.S. production using this process was suspended with increasing natural gas prices, but then resumed when crude oil prices also began to rise. Total energy losses for this process (3,632 Btu/lb) are about half those of the other two ethylene processes, and exergy losses are also significantly lower for this ethane process. However, these losses are given per pound of ethylene product, and the naphtha- and propane-based processes yield more valuable co-products, such as propylene, pyrolysis gasoline, and fuel gasses. Some of the difference may also be due to modeling, as the analysis of this ethane process is based on a more detailed Aspen model than the other two processes. The largest energy loss is from a propylene condenser in the refrigeration section. This is the last in a series of methane, ethylene, and propylene refrigeration compressors, each of which cools against the next cooler circuit. The last condenser represents the energy loss for the whole group of compressors, and has an energy quality of only 2%, indicating no further energy recovery is possible. Other large energy losses are also of fairly low quality. The main internal exergy loss is from the cracking furnace, which has a large temperature difference between process fluid entering the furnace and burner gasses.



Ethylene from Ethane Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Thermal Cracking	495	14	39	1602	1641	48
Compression	1245	34	120	338	459	13
Refrigeration	1888	52	67	891	958	28
Demethanization	0	0	0	103	103	3
Deethanization	4	0	0	100	100	3
Purification	0	0	0	152	152	4
<b>TOTALS</b>	<b>3,632</b>	<b>100</b>	<b>226</b>	<b>3186</b>	<b>3413</b>	<b>100</b>

## Chlorine

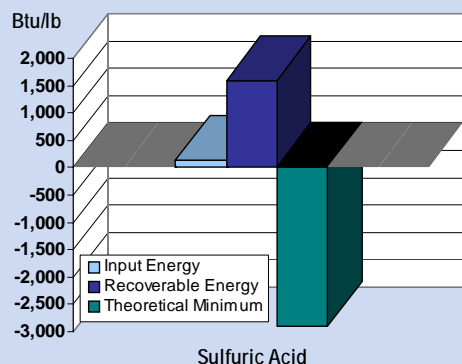
Almost all chlorine is produced by the electrolysis of brine, and most U.S. producers use the diaphragm electrolysis cell modeled here. Two other cells are also used: mercury cells, which are gradually being replaced due to environmental concerns, and newer membrane cells, which have not yet grown to dominate the market. Electrolysis produces chlorine together with by-products sodium hydroxide (caustic soda) and hydrogen, with a theoretical minimum energy of 3,086 Btu/lb chlorine. All the energy and exergy values below are given per pound of chlorine; if energy and exergy losses were also allocated to caustic soda, these figures for chlorine would be lower. In this electrolysis process, the actual input of electrical energy is almost three times the theoretical minimum, and this does not include electrical transmission and generation losses. Energy and external exergy losses are low; most of the exergy losses are internal losses due to irreversibilities in the electrolysis cells.



Chlorine Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Brine	663	69	23	40	63	1
Electrolysis	0	0	0	6395	6395	91
Gas Treatment	227	23	13	232	246	3
Liquor	77	8	0	359	359	5
<b>TOTALS</b>	<b>967</b>	<b>100</b>	<b>36</b>	<b>7026</b>	<b>7063</b>	<b>100</b>

## Sulfuric Acid

About 90% of U.S. sulfuric acid is produced from virgin sulfur, as in this process. The sulfur is burned to produce sulfur dioxide, which is then oxidized to sulfur trioxide. The sulfur trioxide is absorbed in water to produce sulfuric acid. These reactions are very exothermic, and the reaction energy is used to produce 2.7 lb of high pressure steam per pound sulfuric acid. There are very few energy or external exergy losses because of the steam recovery. Almost all the exergy losses are internal exergy losses, and almost 70% of these internal losses are due to irreversibilities in the sulfur roasting section. The sulfur roaster and waste heat boiler in this section operate at high temperatures and have input and output streams at widely different temperatures and conditions.

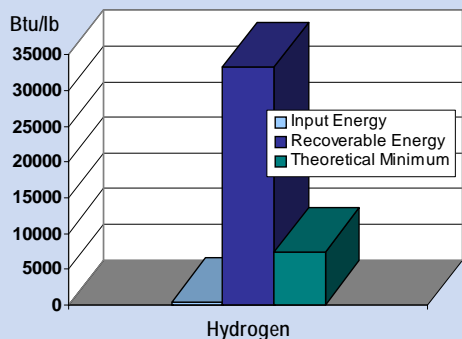


Sulfuric Acid Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Sulfur Roasting	0	0	0	1096	1096	69
SO <sub>3</sub> Production	41	10	25	112	137	9
Product Conversion and Separation	379	90	19	339	358	23
<b>TOTALS</b>	<b>420</b>	<b>100</b>	<b>44</b>	<b>1547</b>	<b>1591</b>	<b>100</b>

## Hydrogen

Hydrogen is produced primarily by steam reforming of natural gas, such as the process modeled here. Hydrogen production by steam reforming is an endothermic reaction with a minimum theoretical requirement of 7,391 Btu/lb. Only a small fraction of this requirement is provided by an external energy input; the remainder comes from combustion of part of the natural gas feedstock, which provides a large reaction energy input. This combustion is used to generate high pressure steam, but there are additional energy recovery opportunities.

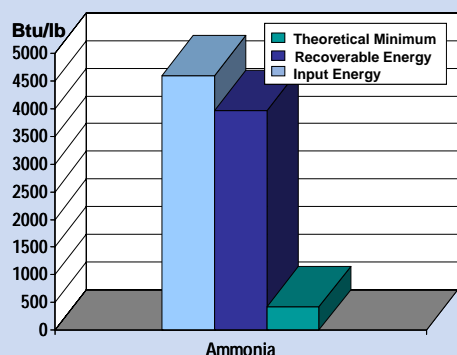
The largest exergy losses occur in the reforming furnace, where the gas combustion products are used to heat steam and preheat other process streams. There is a wide variation in the various streams entering and leaving this unit, resulting in the large internal exergy losses shown. The stack gases constitute 27% of the energy losses, but have been cooled to 350°F and so only account for 2% of the total exergy loss. External exergy losses in the product recovery section are largely from a reformer gasses cooler, where process gasses are cooled from 323°F to 223°F with cooling water. This energy lost to the cooling water has a quality of 27%, and could potentially be used to warm some other process stream instead.



Hydrogen Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reforming section	60	0	37	21545	21583	66.3
Reforming section stack	6342	27	633	135	768	2.3
Product recovery	17196	73	3071	7381	10452	31.4
<b>TOTALS</b>	<b>23598</b>	<b>100</b>	<b>3741</b>	<b>29576</b>	<b>33317</b>	<b>100</b>

## Ammonia

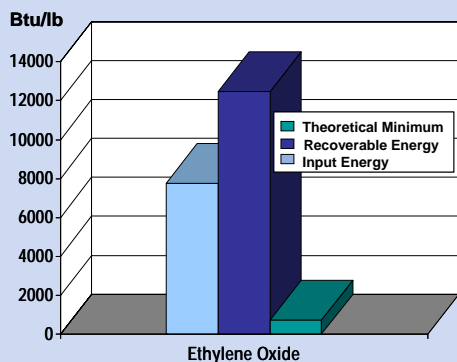
This process is based on a composite of current technologies which have been operating for many years but have seen improvements in catalysts, synthesis upgrading, and energy recovery. Total process energy is about 11 times greater than the theoretical minimum energy requirement for the exothermic ammonia conversion reaction. The synthesis gas separator in the gas upgrading section is the largest source of energy and external exergy losses. This two- or three-column amine unit removes a stream of hot, water-saturated carbon dioxide, which is responsible for large energy losses. The next largest source of energy loss is ammonia synthesis, occurring in the high pressure syngas compressor, syngas reactor, and cooling and refrigeration units. Much of the loss is low-quality energy due to low temperature levels. In preheating and reforming, large internal exergy losses occur in the secondary reformer and waste heat boiler downstream of the reformer. These losses occur due to large temperature gradient-driven heat transfer operations. Considerable waste heat recovery is already used.



Ammonia from Natural Gas Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Preheating/Reforming	556	10	206	1272	1478	38
Shift	0	0	0	164	164	4
Gas Upgrading	2608	49	614	182	796	20
Ammonia Synthesis	1897	36	269	1081	1350	35
Heat Recovery	263	5	81	25	106	3
<b>TOTALS</b>	<b>5324</b>		<b>1170</b>	<b>2724</b>	<b>3893</b>	

## Ethylene Oxide

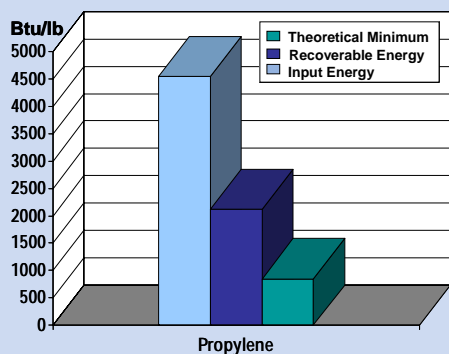
This is an exothermic process based on the Shell process for direct oxidation of ethylene with oxygen (various others are used commercially). Most ethylene oxide plants also produce ethylene glycol in an integrated flowsheet. The process as modeled has half of the product ethylene oxide as an aqueous stream. This has contributed to unusually high energy and exergy losses. In addition, the process as modeled couples the upstream stripping column condenser with the purification column condenser, creating a very large condensing load at a temperature too low for energy recovery. This may not be the common practice. Total process energy is about 10 times theoretical minimum energy requirements. The ethylene oxide purification unit accounts for 91% of energy losses and 19% of exergy losses. In the stripper section, high internal exergy losses are due to heat exchangers and columns in the recirculating water loop. Relatively low temperatures result in little opportunity for heat recovery. Internal losses could be reduced by increasing the areas of the heat exchangers. Large internal losses in the reactor section are due to large temperature differentials between the inlet gas and exothermic conditions in the reactor.



Ethylene Oxide (Shell) Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Feed Pre-Heat	252	2	28	1010	1039	8
Reactor	0	0	0	4163	4163	33
EO Absorber	0	0	0	885	885	7
EO Stripper	985	7	277	3705	3982	32
EO Purification	12352	91	1792	596	2388	19
<b>TOTALS</b>	<b>13588</b>		<b>2096</b>	<b>10360</b>	<b>12456</b>	

## Propylene

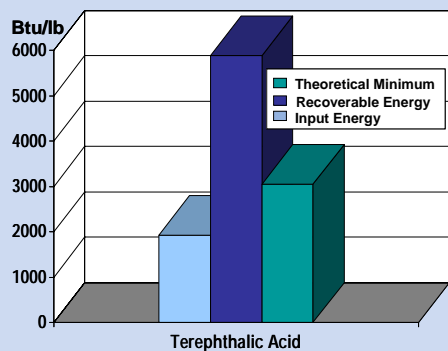
This endothermic process is based on the Fina technology for production of propylene from light naphtha fractions (described in the patent literature but not yet commercialized). Most propylene is now produced as a co-product of ethylene in naphtha crackers, and it is uncertain if dedicated production of propylene from naphtha will ever be commercially popular. It is included here to provide a perspective on innovation. Total process energy is about 5 times greater than the theoretical minimum (ethylene production is 12-13 times greater than theoretical minimum). Most energy losses occur during production separation, mostly due to debutanizer column and coolers. Some level of energy recovery may be possible in this section. The largest exergy loss occurs in the reactor subsection, mostly occurring in the feed preheater, coolers, and the reactor. Large internal losses in this section are due to wide differences in input and output stream temperatures.



Propylene from Naphtha Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Reactor	133	7	21	1513	1534	72
Product separation	1318	74	191	292	482	23
Product purification	293	16	15	22	37	2
By-products	41	2	1	66	67	3
<b>TOTALS</b>	<b>1786</b>		<b>227</b>	<b>1892</b>	<b>2119</b>	

## Terephthalic Acid (PTA)

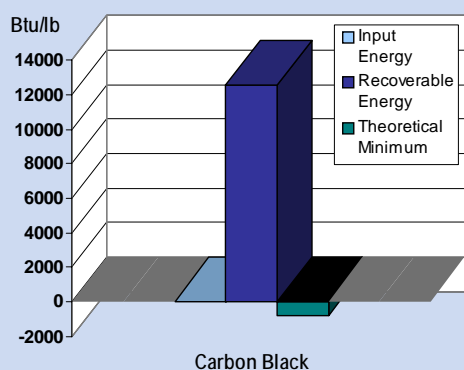
This exothermic process is based on Amoco technology for producing purified terephthalic acid (PTA) via oxidation of p-xylene. It is a complex, energy- and exergy-intensive process. Purification requirements are critical and the current process yields are high. The total process energy input is about twice the theoretical minimum. Large exergy losses occur in the reaction system, mostly due to process irreversibilities associated with the wide range in temperatures and compositions of the various oxidation reactor feed streams and effluent. The oxidation reactor is a main source of losses. In crystallization, the solvent dehydrator is a primary source of losses. Condensers and slurry vessels account for losses during purification. The high selectivity of the current catalyst system limits the interest in seeking new approaches to producing PTA. Current research is concentrated on further improvements to product purification.



Terephthalic Acid from p-Xylene Oxidation Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Oxidation	1943	36	657	3635	4292	73
CTA Crystallizer	1766	33	288	273	561	10
Hydrogenation	49	1	11	435	446	8
PTA Purification	1616	30	484	104	588	10
<b>TOTALS</b>	<b>5374</b>		<b>1440</b>	<b>4447</b>	<b>5887</b>	

## Carbon Black

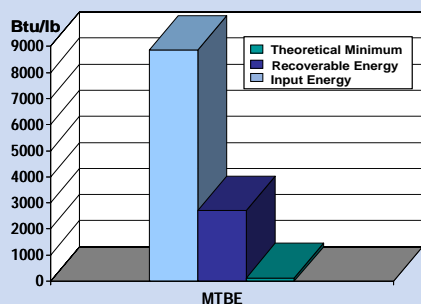
Carbon black is a very fine, fluffy powder of essentially elemental carbon, used mainly to reinforce rubber. Almost all U.S. production uses this oil furnace process, in which oil is decomposed at high temperature to carbon and hydrogen. Part of the oil feedstock is oxidized with air to maintain the process temperature, and the reaction products are quenched with water to prevent the carbon black from reacting with the products of combustion. The high temperature reaction section is used to generate 3.4 lb of high-pressure steam per pound carbon black. Hot effluent gasses are used to preheat the combustion air, but then leave the plant and are modeled as an energy loss (accounting for the entire process energy and external exergy losses). These effluent gasses still have a considerable heating value because of their hydrogen and carbon monoxide content and moderately high temperature. The process flow-sheet does indicate that they are fed to downstream boilers and incinerators outside the process. The remaining exergy losses are mainly due to irreversibilities in the reaction section. The high-temperature furnace and quenching operations are highly irreversible and account for about 70% of the internal exergy losses.



Carbon Black Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reaction & Filtration	0	0	0	10103	10103	80
Purification Separation & Pelletization	8704	100	939	1524	2463	20
<b>TOTALS</b>	<b>8704</b>	<b>100</b>	<b>939</b>	<b>11627</b>	<b>12566</b>	<b>100</b>

## MTBE (methyl tert-butyl ether)

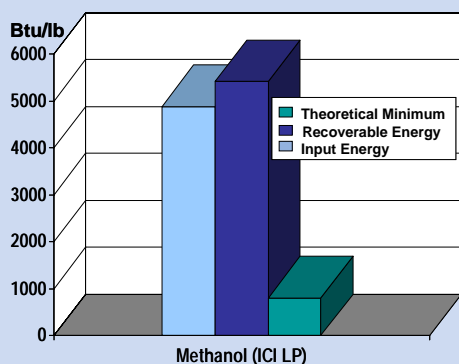
This exothermic “first generation” process uses a liquid acid to catalyze the etherification of isobutylene with methanol. Other technologies in use today use an acid ion exchange resin catalyst in a reactor or within a distillation column (catalytic distillation). The total process energy input is more than 70 times greater than the theoretical minimum energy requirements. Nearly all energy and exergy losses occur in the MTBE recovery section, primarily due to the MTBE distillation column which has a large condensing load. Contributing factors are the low temperature of the overhead streams which require cooling water, and large temperature differences among the overheads, feed, and bottoms stream temperatures.



MTBE Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reactor	297	3	26	137	163	6
Methanol Recovery	63	1	9	7	16	1
MTBE Recovery	8744	96	1373	1155	2527	93
<b>TOTALS</b>	<b>1786</b>		<b>227</b>	<b>1892</b>	<b>2119</b>	

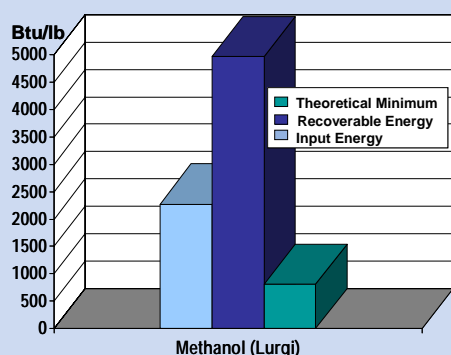
## Methanol

**ICI LP** – This exothermic process is based on the ICI low-pressure technology that includes steam reforming of natural gas, high pressure synthesis of methanol, and distillation for product recovery and separation. The total process energy input is about 6 times the theoretical minimum energy requirement. The sources of large exergy losses in the refining section are a primary distillation column and large heat exchanger. The reforming furnace has large internal exergy losses, primarily due to large differences in temperature of inlet and effluent streams and combustion gases.



Methanol from Natural Gas (ICI LP) Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reforming section	176	2	8	2,791	2,799	52
Synthesis section	313	3	47	516	562	10
Refining section	9,391	95	1,234	822	2,056	38
<b>TOTALS</b>	<b>9880</b>		<b>1289</b>	<b>4128</b>	<b>5416</b>	

**Lurgi** – This process varies from the ICI LP process in that it utilizes a combined reforming process with two stages of reforming in series, the second with oxygen injection. Process energy input is about 3 times greater than the theoretical minimum energy requirement. The heat recovery section exhibits the greatest external exergy losses and indicates the potential for significant energy recovery if low temperature users were available. The methanol column in the refining section also makes a large contribution to energy losses, although it is lower than the similar column in the ICI process. Condenser steam generation could reduce energy losses. Relatively large losses are also attributed to a process exchanger and combustion furnace in the reforming section, and to methanol reactors, condensers and air coolers in the synthesis section. The process exchanger is a candidate for steam generation with substantial energy recovery. The combustion furnace has a lower energy loss but the high external energy ratio suggests the possible use of a waste heat boiler to recover energy. Exergy losses occur in the reforming and heat recovery sections due to the wide range of inlet and outlet temperatures involved. Large temperature differences are also responsible for significant internal exergy losses in the synthesis section.

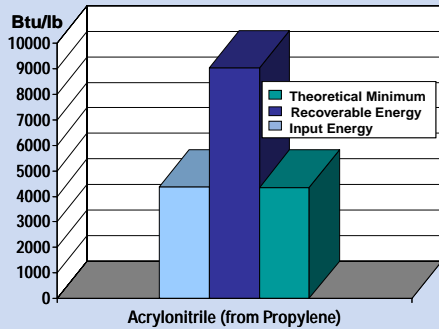


Methanol from Natural Gas (Lurgi) Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reforming section	1483	20	608	2131	2739	55
Synthesis section	1918	25	471	489	960	19
Refining section	1234	16	164	98	262	5
Heat recovery	2958	39	922	99	1021	20
<b>TOTALS</b>	<b>7594</b>		<b>2165</b>	<b>2816</b>	<b>4982</b>	



## Acrylonitrile

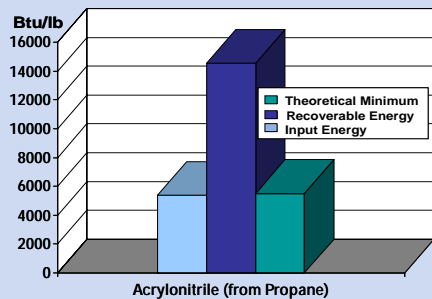
**SOHIO-BP Propylene Ammoxidation** – This exothermic process is based on the SOHIO-BP fluidized bed ammoxidation process, which is now used predominantly for the production of acrylonitrile (ACN). The total process energy input is approximately the same as the theoretical minimum energy required (considerable energy is produced by the exothermic reaction). About 45% of energy losses are recoverable heat and refrigeration of process effluent streams. The largest energy and exergy losses occur in the heat and refrigeration section, primarily due to effects of refrigeration cycles needed to separate the product and byproducts at low temperatures. A large source of losses in the ammoxidation section is the quench column overhead cooler, although most exergy losses occur as internal losses in the ammoxidation reactors due to the large number of input and output streams at widely different temperatures. Increased heat exchange to increase the cold feed temperatures could reduce these irreversibilities, if economic. Most of the losses in the acrylonitrile separation are due to a stripper column and condenser, which is cooled with refrigeration and is very energy-intensive.



Acrylonitrile by Propylene Ammoxidation (SOHIO-BP) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Propylene Ammoxidation	3624	24	354	4238	4592	51
Acrylonitrile Separation	4729	31	404	1599	2003	22
Heat & Refrigeration Recovery	6727	45	2435	5	2440	27
<b>TOTALS</b>	<b>15081</b>		<b>3193</b>	<b>5842</b>	<b>9035</b>	

**SOHIO-BP Propane Ammoxidation** – This exothermic process has not been commercialized. The total process energy input is approximately the same as the theoretical minimum energy requirement. The energy input and losses are similar to those of the process above, but this propane process has a slightly higher energy input, and the quality of the input energy is also higher.

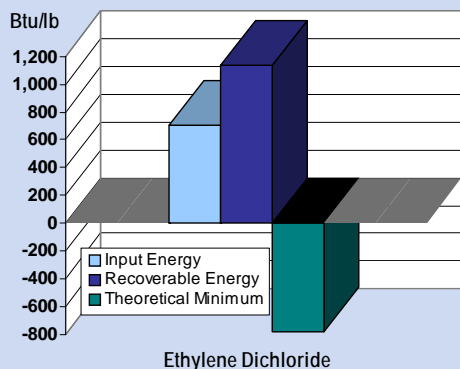
This propane process is similar to the propylene ammoxidation process, but differences in reaction system performance lead to changes in downstream processing. Being more exothermic, the propane process offers more opportunity for steam generation, but is subject to more process irreversibilities due to conversion at higher temperatures. The internal exergy losses in the propane process ammoxidation reactor are almost double those in the propylene process. The propylene process is more selective and has lower exergy losses related to production, separation, and cooling of by-products. This propane process requires more energy for compression and by-product separation; this reflects the larger gas circulation rate caused by lower per pass conversion.



Acrylonitrile by Propane Ammoxidation (SOHIO-BP) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Propane Ammoxidation	3966	27	335	9784	10119	70
Acrylonitrile Separation	5337	36	455	1622	2077	14
Heat & Refrigeration Recovery	5516	37	2339	9	2349	16
<b>TOTALS</b>	<b>14823</b>		<b>3129</b>	<b>11415</b>	<b>14544</b>	

## Ethylene Dichloride

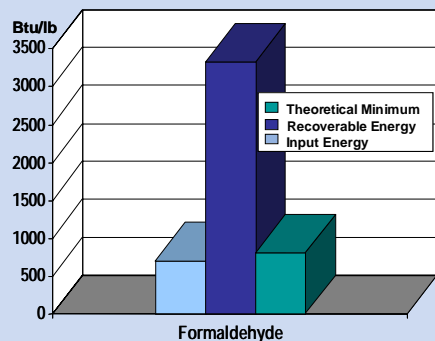
This process is the oxychlorination of ethylene by hydrogen chloride in a fluidized bed using air. Several other versions of oxychlorination technology are also used in the United States. This process uses steam generation for energy recovery in the reactions section and in the gas treatment section, where an incinerator removes all hydrocarbons and waste chlorinated hydrocarbons from the vent gas stream. The exothermic oxychlorination reactor generates 5.3 lb of 25 psig steam per pound product, and the gas treatment section generates a further 1.0 lb per pound product. Energy losses in the purification section are from distillation columns, and are of too low quality for steam generation. The high-temperature reactor and incinerator units account for over 75% of the internal exergy losses.



Ethylene Dichloride Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reactions	648	53	50	794	843	74
Purification	521	42	31	14	45	4
Gas Treatment	62	5	0	251	251	22
<b>TOTALS</b>	<b>1231</b>	<b>100</b>	<b>81</b>	<b>1059</b>	<b>1139</b>	<b>100</b>

## Formaldehyde

This exothermic process produces formaldehyde from methanol using a silver-based catalyst, and is based on BASF technology. (A second technology using a mixed oxide catalyst is also widely used.) The total energy from the process input and from the reaction is about 4 times greater than the theoretical minimum energy requirement. In this relatively simple process configuration, the low temperature quench of the reactor effluent is responsible for most of the energy consumption as well as energy and exergy losses. The very large driving forces around the exothermic reactor contribute to the substantial internal exergy losses.

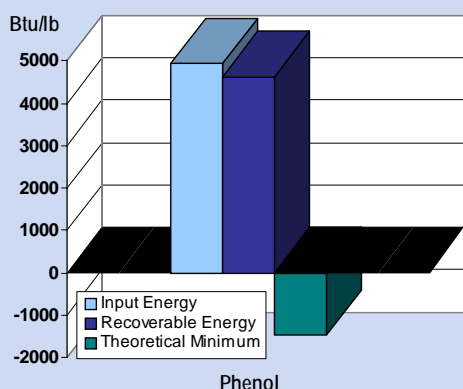


Formaldehyde from Methanol Process Sub-Section	Energy Loss		External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Feed Air/Recycle Air Mixer	0	0	0	19	19	0.56
Feed Air Compressor	0	0.0	0	17	17	0.51
Feed Heater	0	0.0	0	97	97	2.91
Reactor	2268	94.8	487	2463	2950	88.9
Absorber	0	0.0	0	235	235	7.07
Recycle Air Purge	124	5.2	4	2	6	0.19
<b>TOTALS</b>	<b>2392</b>		<b>491</b>	<b>2833</b>	<b>3324</b>	

## Phenol

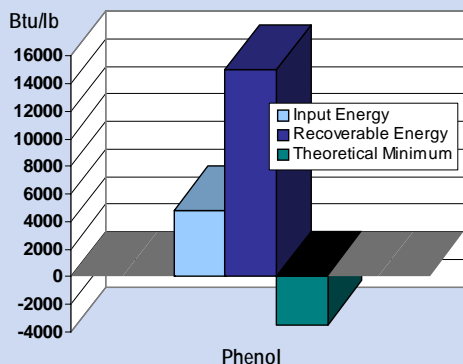
**Oxidation of Cumene** – All major U.S. phenol producers use this process, which generates 0.62 lb of acetone for every pound of phenol. The process is based on two exothermic reactions: cumene is first oxidized to its hydroperoxide, which is then decomposed into phenol and acetone. The reactions occur at relatively low temperatures and the process does not offer much opportunity for energy recovery. If the process could be safely run at a higher temperature with a less active catalyst, there may be more opportunity for useful steam generation.

The main energy losses in the cumene oxidation section occur in two distillation column concentrator units. These are operated at a vacuum due to the hazardous nature of cumene hydroperoxide. The energy quality is low and the overheads temperatures are too low for steam cooling. Energy losses in the product recovery section are also largely in separation columns with no good opportunity for steam generation. Two thirds of the exergy losses in the product recovery section occur in a product cooler unit, where phenol is cooled by tempered water. The tempered water is considered a process stream, so the associated exergy change is an internal loss.



Phenol Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Cumene Oxidation	1841	30	219	254	473	10
Cleavage Section	152	2	10	1014	1024	22
Product Recovery	4065	66	850	2233	3083	67
Water Treatment	51	1	10	4	14	0
AMS Hydrogenation	81	1	21	10	31	1
<b>TOTALS</b>	<b>6190</b>	<b>100</b>	<b>1110</b>	<b>3515</b>	<b>4625</b>	<b>100</b>

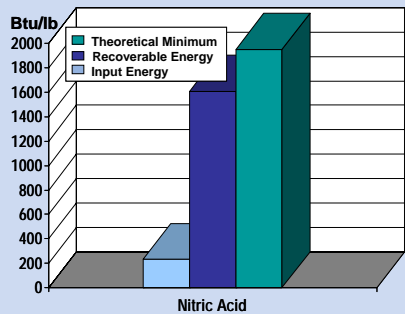
**Oxidation of Toluene** – The dominant cumene production process for phenol produces a fixed ratio of co-product acetone, but the demand for acetone is growing slower than the demand for phenol. In light of this trend, several processes for producing phenol without co-product are under development. This process has been commercialized in one U.S plant, and is based on toluene, a feedstock with a lower and more stable price than cumene. The toluene is first oxidized to benzoic acid, which is then oxidized to phenol via phenyl benzoate. The reactions are all exothermic and generate considerably more energy than the cumene oxidation process above. The reaction energy is used much less efficiently here, so the total energy input for this process is roughly equal to the cumene process. The two largest high-quality energy losses are in the toluene oxidation section. The toluene oxidation reactor and cooler account for 35% of total energy losses, but there is little opportunity for energy recovery or for using low pressure steam in the process.



Phenol Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Toluene Oxidation	6827	63	1831	4603	6434	43
Phenol Production & Separation	3954	37	524	8050	8574	57
<b>TOTALS</b>	<b>10781</b>	<b>100</b>	<b>2355</b>	<b>12653</b>	<b>15008</b>	<b>100</b>

## Nitric Acid

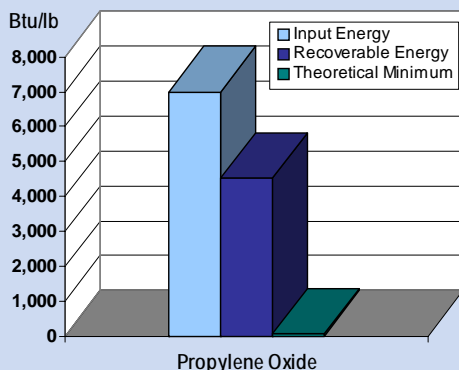
This exothermic process is based on a composite of various licensed technologies for production of nitric acid via oxidation of ammonia to nitric oxide and ultimately nitric acid. The total process input energy is less than the theoretical minimum due to significant energy generation from the exothermic reaction. The largest energy and exergy losses are in the heat recovery section, which appears to have considerable additional capacity for energy recovery. The details of this section are not included in the model. In addition, most nitric acid plants utilized a steam turbine and gas expander to drive one or more compressors, and these are not modeled. Energy losses in the reaction section are due primarily to the nitric acid absorber, where nitrogen dioxide is absorbed in and reacts with water to form form nitric acid, generating heat in the process. The heat of reaction is taken out in the partial condenser of the absorber, usually with refrigeration. Large internal exergy losses are due mostly to extreme temperature differences between feed and effluent streams and other exchanged streams in the system (gas coolers, steam superheaters, evaporators).



Nitric Acid via Ammonia Oxidation Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Reaction	442	20	73	869	942	59
Product Separation	689	31	10	227	237	15
Heat Recovery	1,100	49	409	20	430	27
<b>TOTALS</b>	<b>2230</b>		<b>492</b>	<b>1117</b>	<b>1608</b>	

## Propylene Oxide

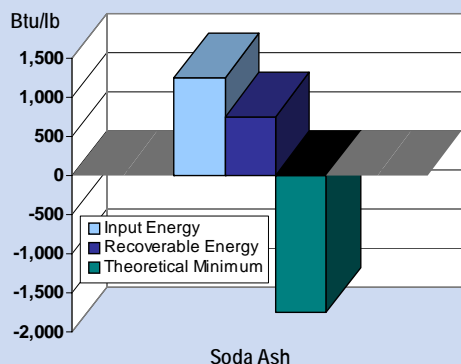
This process produces propylene oxide and tertiary-butyl alcohol (TBA) by oxidizing isobutane to its hydroperoxide and using this hydroperoxide to epoxidize propylene. Similar hydroperoxide processes are used to produce 60% of the U.S. propylene oxide supply, while the remainder is produced using chlorohydrin processes. Producing propylene oxide directly from propylene and isobutane requires a theoretical energy input of 54 Btu/lb, but the reactions in this modeled process generate 2,868 Btu/lb. It is important to note that all the energy consumption and loss values are given per pound of propylene oxide, even though 2.5 lb of TBA are produced for every pound of propylene oxide. The reactions in this process are conducted at low temperatures to minimize side reactions and optimize for the production of propylene oxide and TBA. The low temperature limits energy recovery opportunities, and only a minimal amount of low-temperature steam is generated. Distillation columns account for over 90% of the energy losses, but the temperatures of overhead streams are too low to allow steam generation. The oxidation and epoxidation reactors account for most of the internal exergy losses.



Propylene Oxide Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Isobutane Oxidation	2275	0	215	2048	2262	0
Propylene Epoxidation	151	0	42	1123	1166	0
Product Separation	3458	0	244	431	674	0
PO Purification	1598	0	124	171	296	0
TBA Treatment	92	0	28	100	128	0
<b>TOTALS</b>	<b>7,574</b>	<b>100</b>	<b>653</b>	<b>3873</b>	<b>4526</b>	<b>100</b>

## Soda Ash

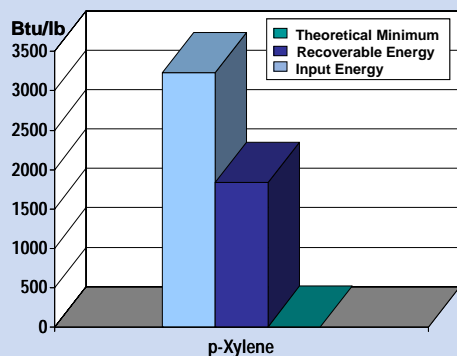
The soda ash (sodium carbonate) process covered here is a modified Solvay process for production from sodium chloride. Little, if any, soda ash is still manufactured using this process; most producers recover soda ash from naturally-occurring deposits or brines. In the Solvay process, sodium chloride is reacted with ammonia and carbon dioxide, and yields almost equal quantities of soda ash and ammonium chloride co-product. About 50% of energy losses occur in a series of carbonation reaction columns in the reaction section. These columns have internal cooling that maintains a low operating temperature and gives little opportunity for energy savings. The same columns are responsible for about 20% of internal exergy losses, with the remainder distributed across various other columns, exchangers, coolers, and crystallizers.



Soda Ash Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Salt Preparation	0	0	0	3	3	0
Crystallizer	344	17	10	200	210	28
Reaction	1152	58	72	343	415	55
Soda Ash Recovery	495	25	53	70	123	16
<b>TOTALS</b>	<b>1,991</b>	<b>100</b>	<b>135</b>	<b>616</b>	<b>751</b>	<b>100</b>

## p-Xylene

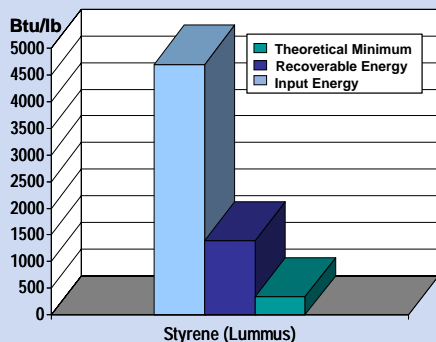
This process is based on conventional technology in which p-xylene is produced from a mixture of C<sub>8</sub> aromatic isomers (p-xylene, o-xylene, m-xylene, ethylbenzene). The isomerization reaction is endothermic, but chemical conversion is exothermic due to side reactions. p-Xylene recovery and purification is not included in the model. The total process input energy is 600 times greater than the theoretical minimum based on isomerization of a p-xylene-depleted xylene mixture. Energy losses are comparable between isomerization and fractionation, but exergy losses are much higher in isomerization due to large temperature differentials between inlet and outlet streams to the reactors and feed preheaters. The low external exergy loss indicates little opportunity for further energy recovery in isomerization. In fractionation, the produce cooler is the largest source of losses. The process temperatures in this cooler are high enough to suggest steam generation or cross-exchange would save energy.



p-Xylene from C <sub>8</sub> Isomers Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Isomerization	1470	56	288	989	1277	70
Fractionation	1165	44	298	260	558	30
<b>TOTALS</b>	<b>2635</b>		<b>586</b>	<b>1249</b>	<b>1835</b>	

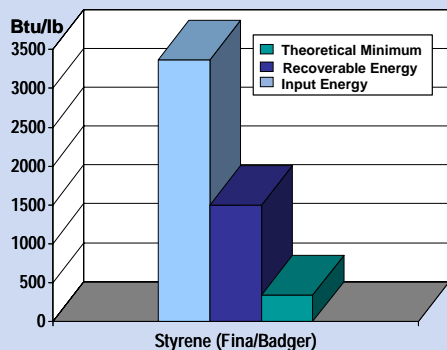
## Styrene

**Lummus/Monsanto/UOP** – This process is based on production of styrene via adiabatic dehydrogenation of ethylbenzene, an endothermic reaction. The total process energy input is about 13 times greater than the theoretical minimum energy requirement. The largest energy losses occur in air coolers, primarily due to inlet and outlet temperature differences. Generating low-pressure steam could reduce these losses, if an economic use for the steam could be identified. Large exergy losses are also found in the feed preheat section, where superheated steam is mixed with fresh and recycle ethylbenzene streams at lower temperatures. Other losses are associated with the steam superheater, stripper units, and fractionators; these are due primarily to large temperature differences leading to process irreversibilities.



Styrene (Lummus/Monsanto/UOP) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Steam Compressor	17	0	17	11	28	2
Steam Super heater	0	0	0	193	193	14
Feed- Preheat/Reactor	0	0	0	371	371	27
Air Coolers	3597	84	408	142	550	39
Condensate Recovery	87	2	5	101	106	8
EB/Styrene Stripper	255	6	21	64	85	6
Styrene Fractionator	261	6	26	17	43	3
EB Stripper	63	1	0	15	16	1
Benzene/Toluene Stripper	7	0	1	1	1	0
<b>TOTALS</b>	<b>4286</b>		<b>478</b>	<b>914</b>	<b>1392</b>	

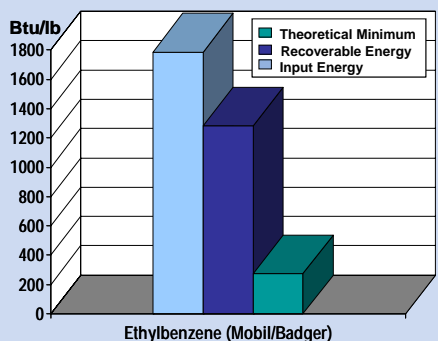
**Fina/Badger** – This endothermic process is very similar to the Lummus process, except for modest differences in the reactor section. The total process energy input is about 10 times greater than the theoretical minimum. The largest energy losses are found in air coolers used to condense and cool the reactor effluent, but the quality of this energy loss is relatively low. The feed preheat accounts for half of the exergy losses, due to large temperature differences in reactor effluent exchangers and in the dehydrogenation reactors. Losses also occur in the ethylbenzene/styrene stripper column, which must be operated under vacuum. The large condenser load for this column is removed with cooling water at a temperature too low for heat recovery. The Lummus process uses a higher steam/ethylbenzene ratio than the Fina/Badger technology, and requires higher energy input. However, the Lummus process recovers low-temperature heat from the ethylbenzene/styrene stripper and exergy losses are lower than those in the same Fina/Badger unit operation.



Styrene (Fina/Badger) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Steam Compressor	1	0	1	0	1	0
Steam Super heater	0	0	0	29	29	2
Feed- Preheat/Reactor	0	0	0	759	759	51
Air Coolers	2716	51	158	48	206	14
Condensate Recovery	125	2	13	77	90	6
EB/Styrene Stripper	1943	37	192	104	296	20
Styrene Fractionator	331	6	33	28	62	4
Benzene/ Toluene Stripper	177	3	13	36	49	3
<b>TOTALS</b>	<b>5293</b>		<b>410</b>	<b>1081</b>	<b>1491</b>	

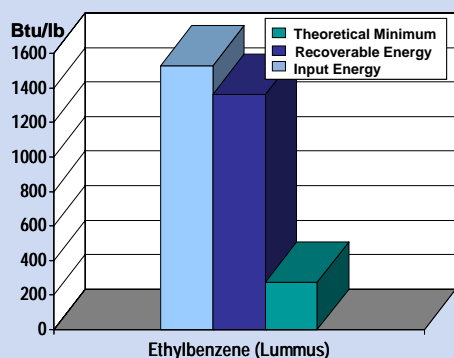
## Ethylbenzene

**Mobil/Badger** – This exothermic process is based on production of ethylbenzene (EB) via vapor phase benzene alkylation. The total process input energy is about 8 times greater than the theoretical minimum. Note that nearly all EB production is integrated downstream with styrene production, and synergies between the two production units are not captured in the stand-alone model used for this analysis. The model also simplifies some of the aspects of the primary reactor and feed preheat to the secondary reactor (an energy-saving feature). The benzene fractionator is the largest source of energy and exergy losses, due to large temperature differences in cooling reactor effluent with incoming feed. There is potential for steam recovery and export in this section. Other sources of losses include the ethylbenzene fractionator and ethylbenzene reactor. The balance of the process is relatively energy-efficient.



Ethylbenzene (Mobil/Badger) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Benzene Fractionator	1850	82	757	267	1024	80
Primary Reactor	0	0	0	108	108	8
Ethylbenzene Fractionator	331	15	92	17	108	8
Poly Ethylbenzene Fractionator	18	1	6	2	7	1
Secondary Reactor	0	0	0	8	8	1
Pre-Fractionator	63	3	16	11	27	2
<b>TOTALS</b>	<b>2262</b>		<b>870</b>	<b>412</b>	<b>1283</b>	

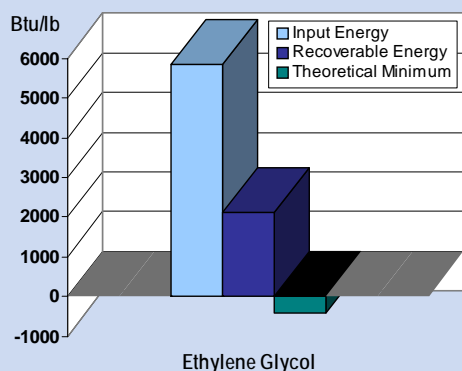
**Lummus** – This exothermic process is based on production of ethylbenzene via liquid phase benzene alkylation, and the front end of the process differs considerably from the Mobil/Badger process. The reaction systems differ substantially in operating temperature as well as phase of reaction. After the reaction system the processes are very similar. Total process energy input for the Lummus process is about 6 times greater than the theoretical minimum, compared with 8 times for the Mobil/Badger process. The benzene fractionator accounts for most energy and exergy losses, similar to the vapor-phase technology. This column processes both fresh feed and recycle benzene, and its large condenser operates at a low temperature, inhibiting economic energy recovery. There is some opportunity for medium- to low-pressure steam export from the alkylation reactor.



Ethylbenzene (Lummus) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Benzene Fractionator	1654	82	501	132	633	46
Primary Reactor	0	0	0	542	542	40
Ethylbenzene Fractionator	344	17	96	13	110	8
Poly Ethylbenzene Fractionator	10	0	3	1	4	0
Secondary Reactor	0	0	0	58	58	4
Pre-Fractionator	0	0	0	16	16	1
<b>TOTALS</b>	<b>2007</b>		<b>601</b>	<b>762</b>	<b>1362</b>	

## Ethylene Glycol

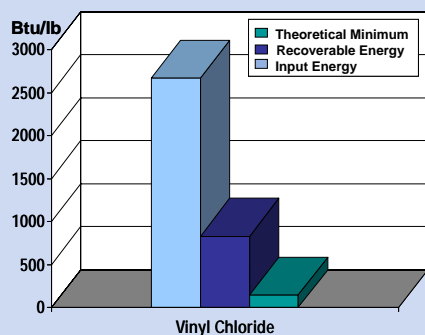
All U.S. producers of ethylene glycol use this thermal hydration process, with variations related to energy efficiency improvements. All U.S. plants are also co-located with ethylene oxide plants, which provide the feedstock and steam for ethylene glycol. This process produces about 10% higher glycols (primarily diethylene glycol) and uses a very high water-to-ethylene oxide feed ratio to minimize the production of these co-products. The hydration reaction is exothermic, but removing excess water from the ethylene glycol product requires much energy. Multiple-effect evaporation is used to reduce the energy requirement: three effects at successively lower pressures, each using the steam driven off from the previous effect as heat source. The final condenser for this evaporation scheme accounts for all the energy losses in the reaction section. The condensing water stream is at 222°F and could potentially be used for process heating. Some larger plants use additional lower-pressure effects, and some plants overseas use catalytic hydration to minimize production of higher glycols and reduce the excess water feed. Energy losses from the purification section are from purification columns, which are operated at low temperatures to protect the product quality. The low condenser temperatures do not allow for further energy savings.



Ethylene Glycol Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reaction	2455	49	521	803	1324	62
Purification	2607	52	376	419	795	38
<b>TOTALS</b>	<b>5062</b>	<b>100</b>	<b>897</b>	<b>1222</b>	<b>2119</b>	<b>100</b>

## Vinyl Chloride

This endothermic process is based on the Hoechst et al. process for gas phase pyrolysis (dehydrochlorination) of ethylene dichloride (EDC). The total process input energy is about 19 times greater than the theoretical minimum energy required. The reaction is carried in the tubes of a fired furnace and the resulting effluent gases are at a higher temperature than input gases. The largest energy losses are in the quench section where reaction effluent is cooled from over 900°F to 120°F, a temperature too low for steam generation. EDC recovery also has high energy losses (source – four distillation columns). The low-pressure HCl column with a refrigerated condenser accounts for losses in the HCl recovery section.

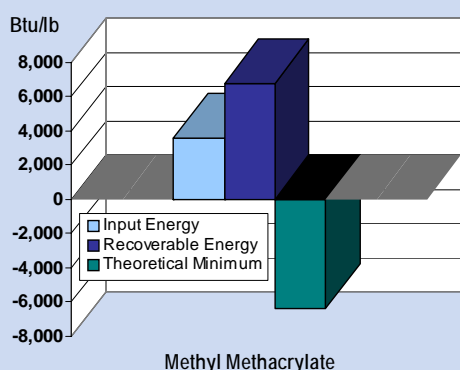


Vinyl Chloride via Gas Phase Pyrolysis Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Pre-Heater	0	0	0	143	143	17
Dehydrogenation Reaction	0	0	0	360	360	43
Quenching	867	42	69	15	84	10
HCl Recovery	281	14	44	24	68	8
VCM Recovery	203	10	10	30	40	5
EDC Recovery	721	35	102	31	133	16
<b>TOTALS</b>	<b>2071</b>		<b>225</b>	<b>603</b>	<b>828</b>	



## Methyl Methacrylate

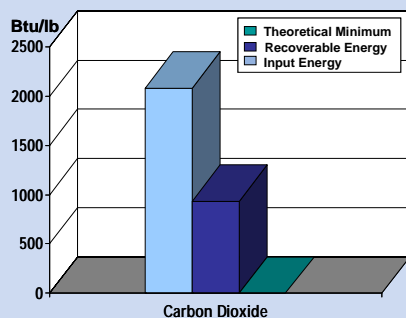
All U.S. methyl methacrylate (MMA) producers use this process in which acetone is reacted with hydrogen cyanide to produce acetone cyanohydrin, which is hydrolyzed with water and sulfuric acid to form methacrylamide sulfate. The methacrylamide sulfate is then esterified with methanol to form the product MMA and 1.3 lb of by-product ammonium bisulfate per pound MMA. The reactions are exothermic, and occur in agitated, liquid-phase reactors with pump-around cooling to maintain moderate reaction temperatures. The esterification reactor is the source of 22% of energy losses and 76% of internal exergy losses. The energy loss is to tempered cooling water with a quality of 22%, and energy savings may be possible with a different cooler recirculation rate. The large internal exergy losses are due to the complexity of the reaction, the higher temperature involved, and wide differences in temperature and composition between the feed streams and the vapor leaving the reactor. The cyanohydration and hydrolysis reactors involve much lower energy and exergy losses; remaining losses are largely associated with distillation columns, with little opportunity for energy savings.



Methyl Methacrylate Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Acetone Cyanohydrin	347	6	29	98	127	2
Hydrolysis & Esterification	4431	82	657	5906	6563	97
Purification	648	12	73	37	110	2
<b>TOTALS</b>	<b>5426</b>	<b>100</b>	<b>759</b>	<b>6041</b>	<b>6800</b>	<b>100</b>

## Carbon Dioxide

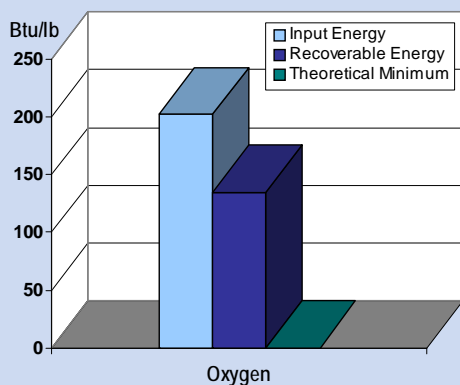
Carbon dioxide is produced by recovery from gas streams where it is a contaminant or by-product. The majority comes from ammonia, hydrogen, or ethylene oxide plants, most commonly using absorption with a physical or chemical solvent. This analysis models a process in which monoethanolamine (MEA) is used to recover carbon dioxide from power plant flue gas. The theoretical minimum energy for a separation is zero, but the actual process requires significant energy inputs. The carbon dioxide stripper and absorber are large sources of energy and exergy losses. A large energy loss occurs where hot flue gas is cooled to minimize water content and temperature of flue gas entering the MEA system. Energy recovery may be possible from the associated cooling water recycle, make-up, and purge loop.



Carbon Dioxide Recovery with MEA Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
CO2 Absorber	377	12	8	478	486	52
Mea-Makeup Mixer	0	0	0	9	9	1
Lean MEA Cooling Exchanger	649	21	58	1	59	6
Rich MEA Solution Pump	0	0	0	0	0	0
Rich/Lean MEA Sol. Exchanger			0	24	24	3
CO2 Stripper	1001	33	171	42	213	23
Feed Quencher Column	0	0	0	40	40	4
Quench/Makeup Mixer/Splitter			24	17	41	4
Lean Mea/Makeup Water Mixer	94	3	12	33	45	5
Quenching Water Cooling Exch.			17	1	18	2
<b>TOTALS</b>	<b>3045</b>		<b>289</b>	<b>646</b>	<b>935</b>	

## Oxygen

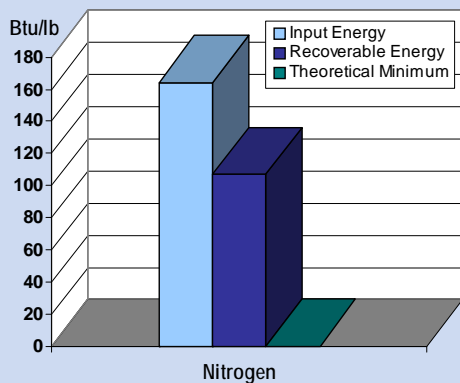
Most of the U.S. supply of oxygen and nitrogen are produced by cryogenic distillation of air. Typically both are produced together, with oxygen as the main desired product in some cases and nitrogen as the product in others. Argon is sometimes separated as a third, and most valuable, product. Some plants produce lower-quality oxygen by membrane separation. The cryogenic process modeled here yields ultra-high purity (99.998%) oxygen, and is representative of many U.S. air separation plants. Cryogenic air separation processes have been highly engineered for energy efficiency through better process integration and heat exchangers. All of the energy loss, and 72% of the exergy losses are associated with the air compressor that feeds the unit and an expansion turbine that expands and cools a portion of the air stream. All heating and cooling in the rest of the process is achieved with Joule-Thomson expansions through valves.



Oxygen Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Compression/Expansion	216	100	14	83	96	72
Purification	0	0	0	37	37	28
<b>TOTALS</b>	<b>216</b>	<b>100</b>	<b>14</b>	<b>120</b>	<b>133</b>	<b>100</b>

## Nitrogen

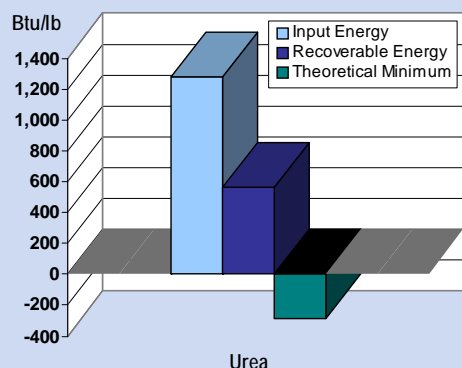
This version of the cryogenic distillation process is designed primarily for producing nitrogen, which does not require as low temperature or high pressure as oxygen. Cryogenic separation is typically used for producing high-purity nitrogen; low-purity nitrogen, or “inert gas,” is sometimes produced by consuming the oxygen content of an air stream and then removing the carbon dioxide produced. A substantial quantity of nitrogen is also produced by membrane separation and pressure swing adsorption (PSA). Like the process for oxygen, the cryogenic process modeled here is very efficient. The only energy input is electrical energy, used primarily to compress the air. Energy losses occur only in the compressor and expander units, while some internal exergy losses are associated with process heat exchangers in the nitrogen purification section.



Nitrogen Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Compression/Expansion	170	100	6	61	67	66
Nitrogen Purification	0	0	0	35	35	34
<b>TOTALS</b>	<b>170</b>	<b>100</b>	<b>6</b>	<b>96</b>	<b>102</b>	<b>100</b>

## Urea

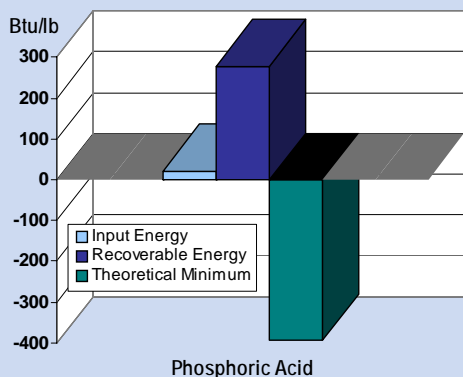
This standard process for urea production is used by all U.S. producers, with minor variations. Ammonium and carbon dioxide react exothermically to produce ammonium carbamate, which is partially dehydrated to urea in the same reactor. The combined reaction is slightly exothermic, generating 63 Btu per pound urea. The process is operated at high pressure but low temperature, so energy losses are relatively low. Most of the energy losses are to cooling water at low temperatures with no potential for energy recovery. Much of the ammonium carbamate intermediate passes through the synthesis reaction, necessitating the most energy-intensive process subsection—carbamate recovery—in which the carbamate is decomposed back into ammonium and carbon dioxide. The largest source of internal exergy loss is a high-pressure absorber used to separate ammonia and carbon dioxide (105 Btu/lb).



Urea Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Synthesis	517	32	47	187	234	41
Purification & Carbamate Recovery	652	40	48	157	205	36
Concentration & Water Treatment	454	28	41	39	80	14
Evaporation & Prilling	5	0	0	47	47	8
<b>TOTALS</b>	<b>1,628</b>	<b>100</b>	<b>136</b>	<b>430</b>	<b>566</b>	<b>100</b>

## Phosphoric Acid

In this process phosphate rock is digested with dilute sulfuric acid to produce phosphoric acid and gypsum as a coproduct (about 3.8 lb per pound of phosphoric acid). Most U.S. producers use this process (with variations in product acid concentration and gypsum hydration), while a few produce phosphoric acid by burning elemental phosphorus. The reactions are exothermic, and this process requires an energy input of only 22 Btu/lb, but this does not include mechanical energy inputs for reduction of ores, washings, solid transports, etc. The sulfuric acid feed is mixed with water, generating heat which is removed by cooling. Almost all the internal exergy losses are caused by this section of the process: the irreversible mixing of two cool streams to generate a high-temperature effluent that is cooled back down to near the cooling water temperature. Almost all the energy and external exergy losses are associated with the acid cooler and have a very low quality. The bulk of the process involves solids and liquid separation and transport, which are low-energy operations.

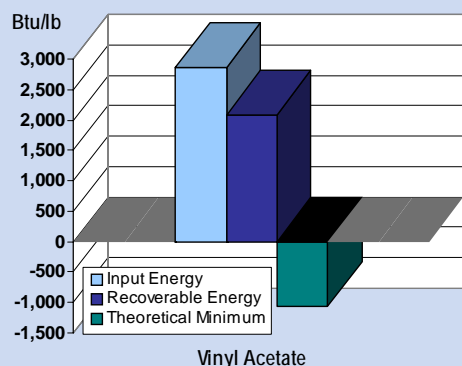


Phosphoric Acid Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reaction	418	88	9	229	238	85
Product Purification	57	12	0	41	41	15
<b>TOTALS</b>	<b>475</b>	<b>100</b>	<b>9</b>	<b>270</b>	<b>279</b>	<b>100</b>

## Vinyl Acetate (VAM)

The vapor phase acetoxylation of ethylene process modeled is a generic one representative of U.S. production. This process includes combustion of ethylene as a side reaction to the main conversion reaction of ethylene with acetic acid and oxygen. These reactions are exothermic and the relatively high temperature and pressure of the reaction leads to significant irreversibilities.

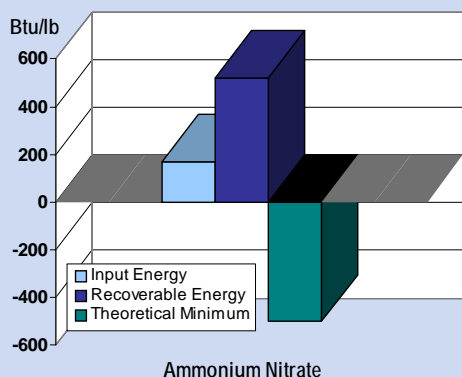
The acetoxylation reactor unit is responsible for the major irreversibilities, and accounts for 53% of exergy losses and 27% of energy losses. The reactor energy losses have a moderately high quality of 30% and are associated with low pressure steam that is generated to maintain the reactor at 302°F but is not used elsewhere in the process. The other significant external exergy loss is from the reactor effluent cooler. This accounts for an energy loss equal to that of the reactor, but at lower quality, with less opportunity for recovery.



Vinyl Acetate Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reaction Section	2656	59	610	1008	1618	78
Vapor Recovery	418	9	88	51	140	7
VAM Recovery	1462	32	218	109	327	16
<b>TOTALS</b>	<b>4536</b>	<b>100</b>	<b>916</b>	<b>1168</b>	<b>2085</b>	<b>100</b>

## Ammonium Nitrate

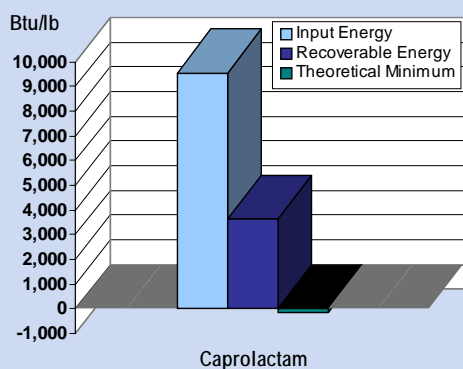
The reaction of nitric acid and ammonia to produce ammonium nitrate is exothermic and requires an energy input of only 171 Btu/lb. But ammonium nitrate is one of the largest volume inorganic chemicals, so the total annual energy use and losses are still significant. The process modeled here produces high-density ammonium nitrate prills and is typical of processes used in almost all U.S. plants. Most of the energy and exergy losses are in the neutralization (reaction) and concentration sections, with the main loop reactor as the largest consumer of both energy and exergy. The other energy losses are losses from relatively low temperature streams to cooling water, with little opportunity for energy recovery.



Ammonium Nitrate Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Neutralization	472	65	117	300	417	80
Concentration	255	35	36	36	71	14
Prilling	0	0	0	29	29	6
Finishing	3	0	0	3	3	1
<b>TOTALS</b>	<b>730</b>	<b>100</b>	<b>153</b>	<b>368</b>	<b>520</b>	<b>100</b>

## Caprolactam

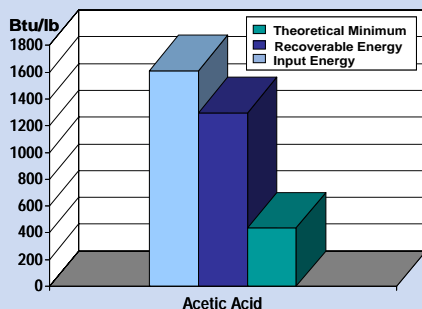
This process consists of two exothermic reactions: cyclohexanone oxime is rearranged with an acidic oleum catalyst and then neutralized with water and ammonia to produce caprolactam along with ammonium sulfate co-product (3.9 lb per pound caprolactam). All three U.S. caprolactam producers use this process, differing mainly in the source of the oxime feedstock (cyclohexane or phenol). The reactors are kept at a relatively low temperature using cooling water, so there is little opportunity for energy recovery. The reactors are responsible for 52% of energy losses and almost 80% of exergy losses. The exergy losses are primarily internal and are caused by the complex reactions and wide range in temperature and conditions of input and output streams. The caprolactam recovery section has significant energy losses to distillation column cooling water, but at low temperatures with little opportunity for energy recovery. The ammonium sulfate recovery section accounts for 65% of process energy inputs, but has very low energy and exergy losses.



Caprolactam Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Oxime Rearrangement	2292	52	203	2658	2861	79
Caprolactam Recovery	1719	39	146	478	624	17
Ammonium Sulfate Recovery	390	9	5	131	136	4
<b>TOTALS</b>	<b>4401</b>	<b>100</b>	<b>354</b>	<b>3267</b>	<b>3621</b>	<b>100</b>

## Acetic Acid

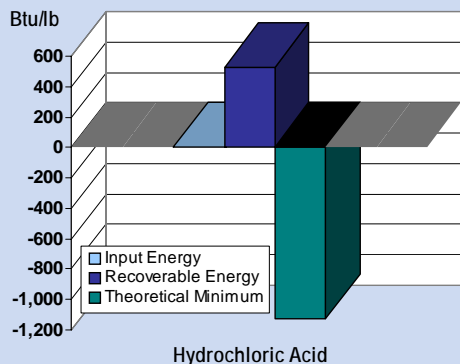
This analysis looks at a new technology (Acetica Process) developed by Chiyoda and UOP that is similar to other acetic acid facilities utilizing carbonylation of methanol. This process differs in the bubble column reactor design, which eliminates the agitator, and in that the catalyst is not dissolved in the reaction medium, but immobilized onto solid particles. No commercial plants are currently operating with this technology. The total process input energy is about 4 times the theoretical minimum energy requirement. Acetic acid refining accounts for the largest energy and exergy losses, primarily due to the crude fractionator. The overhead temperature of the column is too low to reasonably recover the energy in condenser cooling water. Large internal exergy losses are due to large temperature, pressure, and composition differences of the streams leaving the column. Large internal exergy losses are also present in the carbonylation reactor, due to large temperature, pressure, and composition differences among the recycle, feed methanol, and carbon monoxide streams.



Acetic Acid via Methanol Carbonylation Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Carbonylation	118	8	19	715	734	57
Acetic Acid Refining	1326	92	144	419	563	43
<b>TOTALS</b>	<b>1444</b>		<b>163</b>	<b>1134</b>	<b>1297</b>	

## Hydrochloric Acid

Most hydrochloric acid is produced as a co-product from various chlorination processes and is used by the producer for downstream production of organic or inorganic chemicals. Less than 10% is produced on-purpose from hydrogen and chlorine, as in this process for producing 22° Bé (35%) aqueous hydrochloric acid. This exothermic reaction of chlorine and hydrogen takes place in a combustion chamber and produces 530 Btu of reaction energy per pound product. The combustion is responsible for large internal irreversibilities, due to large temperature difference between inlet gasses (125°F), peak internal temperature (4000°F), and outlet gas (400°F). All the external exergy and energy losses are in low-quality cooling water streams, indicating no energy recovery is possible.

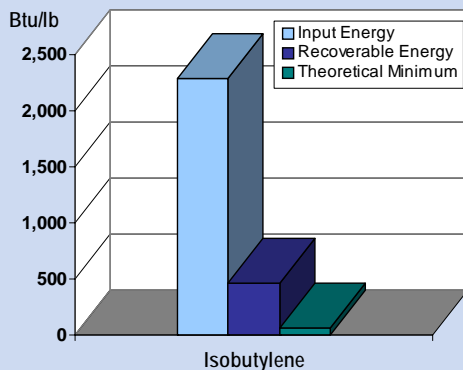


Hydrochloric Acid Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Combustion/Reaction	0	0	0	435	435	82
Reactor Cooler	421	62	10	0	10	2
Absorption	254	38	13	72	85	16
<b>TOTALS</b>	<b>675</b>	<b>100</b>	<b>23</b>	<b>507</b>	<b>530</b>	<b>100</b>

## Isobutylene

The production of isobutylene by dehydration of tertiary butyl alcohol (TBA) does not show large energy or exergy losses. The catalytic reaction is endothermic, and occurs at a relatively low temperature. There are limited opportunities for waste heat recovery through steam generation. It should be noted that most isobutylene is a co-product of olefin production in steam crackers, and other dehydrogenation processes are also used for on-purpose production of isobutylene.

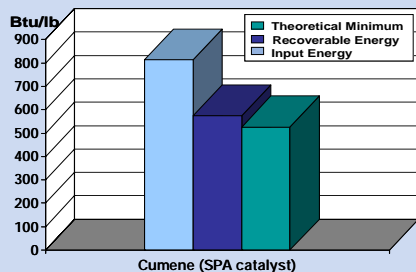
The most significant external exergy loss is in the reactor outlet cooler, which accounts for a third of the external exergy losses in the dehydration sub-section and has a quality of 19%. The front section of this cooler could potentially be used to generate low-pressure steam, but this is not likely to be economical due to the size of the exergy losses. None of the process equipment have significant internal exergy losses.



Isobutylene Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
TBA Dehydration	913	44	83	185	269	58
Purification	1149	56	68	130	197	42
<b>TOTALS</b>	<b>2062</b>	<b>100</b>	<b>151</b>	<b>315</b>	<b>466</b>	<b>100</b>

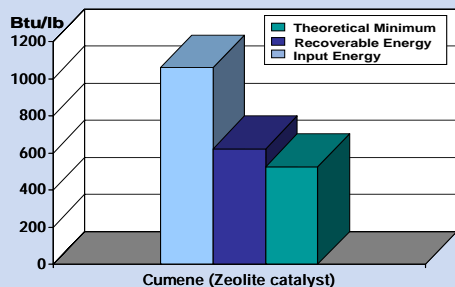
## Cumene

**Solid Phosphoric Acid (SPA) Catalyzed** – This exothermic process is based cumene via propylene alkylation of benzene with an SPA catalyst (UOP design). The total process energy input is about 1.5 times greater than the theoretical minimum. The largest energy losses occur in air coolers, primarily due to their low temperatures. Virtually all energy and exergy losses occur in the cumene recovery section, primarily due to three distillation columns. Additional energy recovery is possible from the cumene fractionator, but may not be economical. There may be opportunity for feed preheat in the alkylation section.



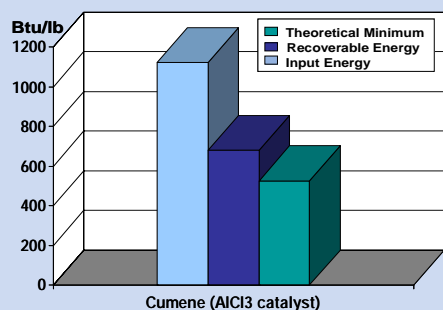
Cumene via Propylene Alkylation of Benzene (SPA-catalyzed) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Alkylation	0	0	0	156	156	27
Cumene Recovery	1170	100	192	225	416	71
<b>TOTALS</b>	<b>1172</b>		<b>192</b>	<b>382</b>	<b>573</b>	

**Zeolite Catalyzed** – The advantage of the zeolite process is that it is non-corrosive and enables operation at lower benzene/propylene ratios, resulting in lower energy and external exergy losses. Recovery of spent catalyst is also easier than the other two processes studied. Fouling of the zeolites, however, could lead to higher catalyst costs. Total process energy input is about 2 times the theoretical minimum. Cumene recovery is again the greatest source of energy and exergy losses, due to several distillation columns, most of which operate at condenser temperatures too low to generate low pressure steam. The cumene column is a candidate for steam generation, with an overhead temperature over 300°F.



Cumene via Propylene Alkylation of Benzene (Zeolite-catalyzed) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Alkylation	231	17	64	187	250	40
Cumene Recovery	1154	83	240	133	373	60
<b>TOTALS</b>	<b>1385</b>		<b>304</b>	<b>319</b>	<b>623</b>	

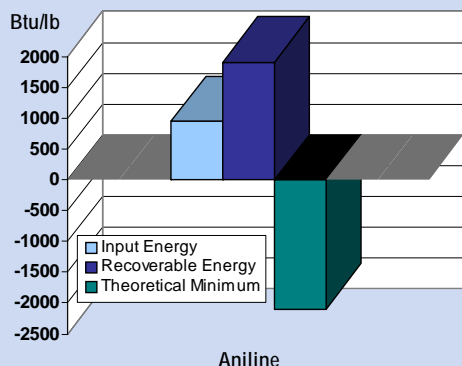
**AlCl<sub>3</sub> Catalyzed** – This process is very similar to the zeolite process discussed above, except that the spent catalyst is not as easy to recover. There are additional minor energy and exergy losses in the catalyst recovery section, which is not required for the zeolite technology.



Cumene via Propylene Alkylation of Benzene (AlCl <sub>3</sub> -catalyzed) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Alkylation	424	28	68	203	271	40
Catalyst Recovery	3	0	0	1	2	0
Cumene Recovery	1104	72	268	139	407	60
<b>TOTALS</b>	<b>1531</b>		<b>337</b>	<b>343</b>	<b>680</b>	

## Aniline

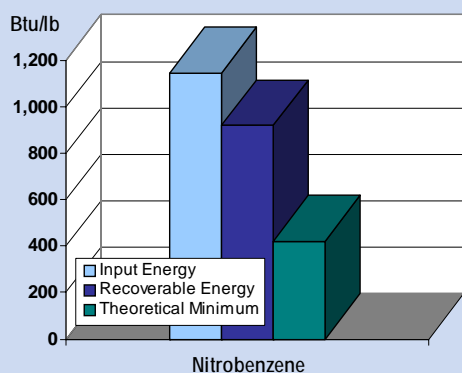
About 95% of U.S. Aniline is produced by the vapor-phase reduction of nitrobenzene, an exothermic process. The reaction energy is used to generate 1.6 lb of 250-psi steam per pound of aniline, such that the process is a net exporter of energy. It could be designed to be energy self-sufficient, though using this generated steam in the process would involve conversion inefficiencies and other losses. Because of the steam generation, the process energy losses are relatively small and of low quality. The largest energy loss is from a cooler that partially condenses vapor exiting the reactor. This unit is the third in a series of coolers, after two exchangers that heat other process streams. Due to the preheating, streams entering and leaving the main fluidized bed reactor are at widely differing conditions, leading to internal exergy losses of 1,512 Btu/lb in the reactor.



Aniline Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reaction	888	72	158	1653	1811	94
Purification	354	29	40	67	106	6
<b>TOTALS</b>	<b>1242</b>	<b>100</b>	<b>198</b>	<b>1720</b>	<b>1917</b>	<b>100</b>

## Nitrobenzene

All five U.S. nitrobenzene plants use processes essentially the same as this liquid-phase nitration of benzene process. Concentrated sulfuric acid catalyst is mixed with the nitric acid reactant, and it is recovered in the last stage of the process. The nitration reactor is responsible for a third of the total energy losses, and almost half of the total exergy losses. The reactor operates at 140°F, a temperature too low for steam generation. There is only one unit that may allow low pressure steam generation. A cooler that accounts for two thirds of the energy loss in the purification section could perhaps be split in two parts, one generating steam and the other using cooling water. The main internal exergy losses are in the nitration reactor, which uses the reactor system to preheat feeds and cool effluents. This is economically attractive, but causes irreversibilities.

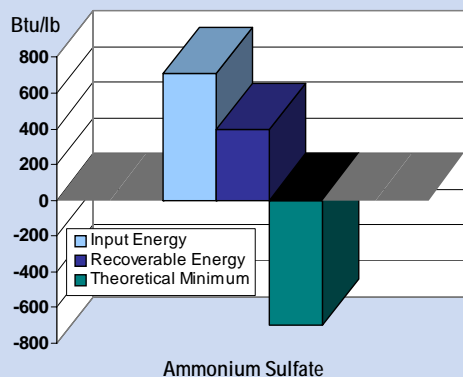


Nitrobenzene Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Nitration	549	39	44	444	489	53
Purification	401	28	50	51	100	11
Sulfuric Acid Recovery	462	33	70	262	333	36
<b>TOTALS</b>	<b>1412</b>	<b>100</b>	<b>164</b>	<b>757</b>	<b>922</b>	<b>100</b>



## Ammonium Sulfate

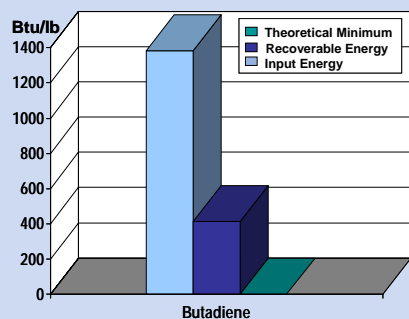
This process is based on the exothermic reaction of gypsum with ammonium carbonate, which is formed by another exothermic reaction of ammonia with water and carbon dioxide. Most U.S. ammonium sulfate producers employ this process to make use of by-product gypsum, but some smaller producers use various other processes. The main gypsum-ammonium carbonate reaction is conducted in agitated vessels at a low temperature, and has an internal exergy loss of 127 Btu/lb due to variations in temperature and composition of the process streams. The rest of the process is also operated at very low temperatures. Essentially all the energy and external exergy losses are associated with cooling water at about 135°F, and do not present opportunities for energy recovery.



Ammonium Sulfate Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Gypsum Reaction	0	0	0	134	135	34
Ammonium Carbonate Formation	392	43	63	56	119	30
Ammonium Sulfate Concentration	520	57	43	101	144	36
<b>TOTALS</b>	<b>912</b>	<b>100</b>	<b>106</b>	<b>291</b>	<b>398</b>	<b>100</b>

## Butadiene

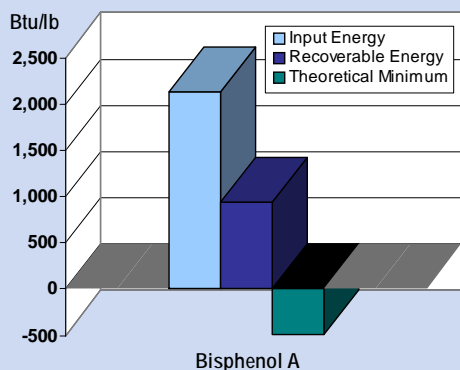
This analysis looks at extractive distillation with DMF solvent (Nippon Zeon process) to recover butadiene from mixed C<sub>4</sub> streams (butane, butene, butylene, and butadiene). Other commercial processes are also used, and differ in the choice of solvent. This extractive distillation process is strictly a separation process with no chemical reaction, so no theoretical minimum is given. Distillation columns (the butadiene stripping column, butene extractive column, propyne and butadiene product columns) account for large energy and exergy losses in extractive and conventional distillation. The large internal exergy losses reflect wide differences in the composition and temperature of inlet and outlet streams. Large energy losses are due to refrigeration used for condensation in some cases. Most of the column condensers are operating at temperatures too low for energy recovery, except the acetylenes stripping column, where reuse of heat of condensation is possible.



Butadiene from C4 Streams Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Feed Vaporizer & DMF Cooling	304	28	9	79	88	21
Extractive Distillation	391	35	13	230	243	59
Conventional Distillation	408	37	21	61	82	20
<b>TOTALS</b>	<b>1103</b>		<b>44</b>	<b>369</b>	<b>413</b>	

## Bisphenol A

This process is for the production of 99.55% purity bisphenol A by the liquid-phase reaction of acetone and phenol, catalyzed by hydrochloric acid. All producers in the United States use this process, with minor variations related to product purification. The reaction is exothermic, but occurs at a low temperature (about 120°F) so internal exergy losses related to the reaction are low. The main internal energy losses are rather in distillation columns with large temperature differences and a burner used for hydrochloric acid recovery. Most of the energy losses are in distillation columns, most of which have low condensing temperatures. There may be some opportunity for heat integration, but energy losses are mainly to cooling water and of low quality.

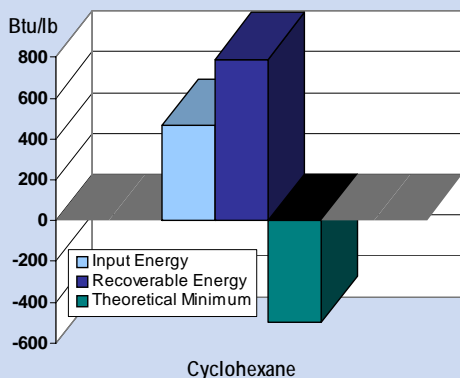


Bisphenol A Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Synthesis	1287	56	174	228	402	43
HCl Recovery	437	19	34	333	367	39
Finishing	593	26	127	42	169	18
<b>TOTALS</b>	<b>2317</b>	<b>100</b>	<b>335</b>	<b>603</b>	<b>938</b>	<b>100</b>

## Cyclohexane

Almost all cyclohexane is produced by hydrogenation of benzene. This hydrogenation reaction is exothermic, and the process requires only a relatively small energy input for pumps, compressors, and reboilers. Cyclohexane also has one of the lowest production volumes of the chemicals studied in this report, so has a low total energy saving potential. This vapor-phase hydrogenation process may be more energy intensive than newer liquid-phase processes, but it is very selective and has little promise for energy savings by improvement of the catalyst or process. Some additional steam recovery is the main opportunity for energy savings.

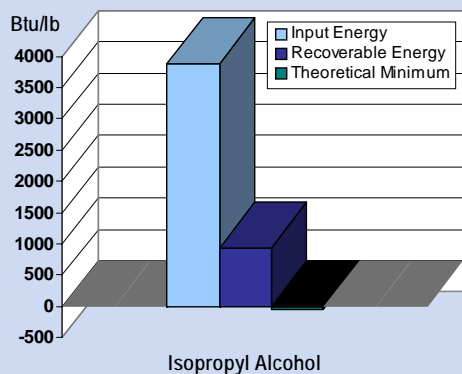
The two reactor units in the reaction section account for the bulk of energy and exergy losses. The main hydrogenation reactor is cooled by generating very low pressure steam, but with no obvious place for the steam to be used. If a less active catalyst were used with a higher process temperature the reaction could generate higher-pressure steam, which may be easier to use.



Cyclohexane Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reaction Section	1317	89	294	455	749	94
Product Purification	171	11	33	11	44	6
<b>TOTALS</b>	<b>1488</b>	<b>100</b>	<b>327</b>	<b>466</b>	<b>793</b>	<b>100</b>

## Isopropyl Alcohol

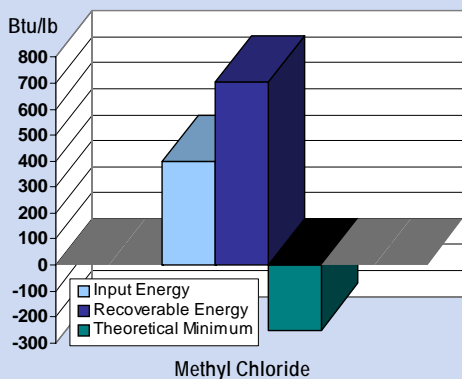
This process is the hydration of propylene to produce equal amounts of premium-grade and lower-purity isopropyl alcohol (IPA). This process uses a cation exchange resin catalyst; most U.S. plants use sulfuric acid as catalyst, an older variation of the process that probably involves higher energy consumption. The hydration reaction is exothermic, but the process uses a considerable amount of energy for purification columns. Almost 90% of the energy losses are from three condenser units in the purification section. These condensers operate at temperatures too low for steam generation and with small temperature differences between condensate and coolant, indicating there is little opportunity for further energy savings.



Isopropyl Alcohol Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reaction	274	6	29	186	215	23
Purification	3954	94	399	318	717	77
<b>TOTALS</b>	<b>4228</b>	<b>100</b>	<b>428</b>	<b>504</b>	<b>932</b>	<b>100</b>

## Methyl Chloride

All U.S. manufacturers of methyl chloride use the exothermic methanol and hydrochloric acid process, and usually produce other chloromethane co-products (methylene chloride, chloroform, and carbon tetrachloride). U.S. Methyl chloride production constitutes relatively small total energy use and losses, but these numbers do not include material produced as a precursor for other chloromethanes or silicones. Over 50% of the energy and internal exergy losses occur in the integrated reactor (reaction section) and rectifying column (purification section) unit. The HCl stripper column (purification section) has energy losses of 271 Btu/lb at a moderate 20% quality. Otherwise energy losses are of low quality, so potential for energy recovery is low without modifications to the process.



Methyl Chloride Process Sub-Section	Energy Loss		External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss	
	Btu/lb	%			Btu/lb	%
Reaction	0	0	0	283	283	40
Purification	1282	100	139	281	420	60
<b>TOTALS</b>	<b>1282</b>	<b>100</b>	<b>139</b>	<b>564</b>	<b>703</b>	<b>100</b>

## Energy/Exergy Losses by Unit Operation

Energy and exergy losses were compiled for unit operations and classes of equipment common to the 53 chemical process technologies. To keep the analysis to a manageable size, only equipment with a duty of 500 Btu/lb or higher was evaluated. Aggregated results for the analysis are shown in Table 6, and more detailed results for each process are shown in the appendix, Table A1. Distillation was found to be the major energy consumer and largest source of energy and exergy losses in the processes analyzed. Exothermic reactors are a significant source of internal exergy losses (process irreversibility losses), while those of distillations include both internal and external losses.

### *Distillation Units*

Distillation is the dominant separation technology and contributes a significant portion of energy/exergy losses. Most of the external exergy losses in distillation units occur in condensers, which are usually cooled by cooling water or air. In many of the processes studied, a relatively few distillation columns and heat exchangers are responsible for the bulk of energy and exergy losses. In some cases a combination of low temperature requirements and non-condensables dictates the use of refrigeration, a large source of energy use and losses. These losses could be minimized by improved heat integration, such as cooling the condensers with other process streams or by using waste heat to raise steam. Another approach is development of alternative separation technologies that do not require raising products to their respective boiling points.

Unit Operation	Energy Loss (TBtu/yr)	Exergy Loss (TBtu/yr)
Endothermic Reaction	0	238
Exothermic Reaction	63	284
Distillation	506	185
Evaporation	16	9
Adsorption/Absorption	22	27
Crystallization	3	2
Cooling Water	1183	162
Heat/Electrical/Steam Energy	1781	1106

### *Exothermic Reactors*

In exothermic reactors, exergy losses are due to the wide range of operating temperatures in feeds and products, and using the reactor to accomplish some portion of feed preheat. Exergy losses could be minimized by lowering operating temperatures or by using waste heat to preheat reactor feeds or generate steam for reuse or export. Improved reaction conversions and selectivities or new reaction chemistries with higher selectivities are possible approaches for reducing these losses. Another option is minimizing reaction exergy losses through changes in process parameters. Lower temperature reaction systems that mitigate the need for quenching of products could also reduce losses in a number of exothermic processes.

### *Separations*

Separations other than distillation, such as evaporation, adsorption, or crystallization, do not contribute substantially to overall energy and exergy losses. However, implementation of more energy-efficient separation technologies could also play a large role in reducing energy/exergy losses in major operations. For example, the use of membrane separation in ethylene production technology could be a viable option to de-methanize or de-ethanize crude ethylene without the need for refrigeration and refrigerated-distillation. Another example is styrene production, where the very high temperature product effluent must be brought to a very low temperature before recovery, with substantial energy use and losses. A novel separation scheme to recover styrene could improve the energy profile.

### *Endothermic Reactions*

Endothermic reactions show zero energy loss because the models are based on effective energy input into each reactor. Large internal exergy losses result from irreversibilities in the reaction and heat transfer to process streams.

Type of Equipment	Number	Energy Loss (TBtu/yr)	External Exergy Loss (TBtu/yr)
Heat Exchangers	48	1174.7	196.1
Distillation Columns	21	447.5	99.4
Reactors	8	69.0	22.7
Furnace & Stack units	4	37.6	6.3
Vessels & Drums	3	41.0	5.0
Compressors	3	14.3	5.0
Other equipment	5	104.4	32.5

Grouping specific equipment types provides a perspective on where energy losses are greatest. As Table 7 illustrates, energy losses are concentrated in heat exchangers and distillation columns (strippers, fractionators). Condensers, air and product coolers, and heat and refrigeration recovery units account for a large share of heat exchanger losses. The column losses shown in Table 7 are also due primarily to heat exchange losses in condensers, which are not always modeled as separate units. In all processes heat exchange accounts for the overwhelming majority of energy and exergy losses.

Table 8 provides details on the eleven unit operations with annual energy losses over 20 trillion Btu for individual chemical processes. Energy quality indicates the potential for energy recovery. As stated earlier, an energy quality of 15%-20% is moderate and indicates some potential for economical energy recovery. For quality over 20%, the potential for economic energy recovery becomes much greater.

Most of the units listed in Table 8 are equipment for distillation and other separations processes. The MTBE distillation column has low overhead temperatures and high losses to cooling water. The Ammonia syn gas separator is also a separations unit, removing carbon dioxide from the product stream. Acrylonitrile separations require refrigeration and quenching, both large sources of energy and exergy losses, and there are significant opportunities for energy recovery (energy quality of 36%).

The ethylene oxide condenser consumes 11,621 Btu/lb, and has by far the highest energy intensity on a per-pound-product basis. This condenser separates the product and water from non-condensables in an overhead stream, with no opportunity for steam recovery. The high energy consumption is also due to the very low per pass conversion of ethylene needed to maintain selectivity, which necessitates scrubbing with water and results in a very dilute overhead stream that makes product recovery difficult.

These results fortify the conclusion that separation processes not requiring distillation could be developed to greatly improve energy efficiency. Alternatively, fundamental process changes could mitigate the need for difficult separations. In some cases better heat integration (e.g., pinch analysis) can be applied to reduce exergy losses. However, this is limited to pure heat exchanger networks involving pure heat load analysis, and cannot be used, for example, to improve a system with heat pumps. In such cases pinch and exergy analysis could be combined to better evaluate targets for improvement.

Technology	Item Name	Energy Loss (TBtu/yr)	External Exergy Loss (TBtu/yr)	Quality (%)
MTBE	MTBE column	110.4	17.3	16%
Ethylene Oxide	Condenser for stripping column	92.9	14.0	15%
Ammonia	Syn gas separator	61.9	14.6	24%
Ethylene (from naphtha)	Air cooler	37.6	4.0	11%
Hydrogen	Reformer gases cooler	28.4	7.7	27%
Methanol (ICI, LP)	No. 3 methanol column	25.2	3.3	13%
Acrylonitrile (from propylene)	Heat & refrig. recovery	23.3	8.4	36%
Ethylene (from naphtha)	Demethanizer column	22.3	7.9	35%
Hydrogen	Stack	20.9	2.1	10%
Formaldehyde	Reactor	20.5	4.4	21%
Hydrogen	Carbonate stripper column	20.2	2.1	10%

Table 9. Energy and Exergy Losses at the Unit Operation Level (Btu/lb)									
Process		Reactions		Separations				Utilities	
		Endothermic	Exothermic	Distillation	Evaporation	Adsorption/ Absorption	Crystallization	Cooling Water	Heat, Electrical, Steam, etc.
Styrene (Lummus)	Energy	0		295				569	4,703
	Exergy	69		129				50	1,697
Vinyl Chloride	Energy	0		1,180				1,200	2,671
	Exergy	360		239				162	975
Ethyl Benzene (Badger)	Energy	0	0	2,126				2,262	1,787
	Exergy	3	23	877				870	965
Ethylene Oxide	Energy		0	441		0		14,630	7,741
	Exergy		4,047	516		903		2,579	5,735
Ethylene (from propane)	Energy	0	34	642		0		2,522	8,656
	Exergy	106	41	1,112		0		345	5,534
Carbon Dioxide	Energy			1,001		377		2,299	2,083
	Exergy			253		486		286	508
Formaldehyde	Energy		0					2,268	698
	Exergy		235					487	115
Ethylene (from naphtha)	Energy	0	0	1,071				4,830	8,139
	Exergy	492	100	1,087				382	5,035
Methanol (ICI)	Energy	0	0	8,017		0		9,601	4,883
	Exergy	54	2,108	3,768		23		1,245	871
Acetic Acid	Energy		0	1,394				1,332	1,612
	Exergy		714	507				138	786
Styrene (Fina/Badger)	Energy	0		2,120				5,193	3,365
	Exergy	248		380				397	1,121
Acrylonitrile (from propylene)	Energy		0	2,923	0	92		5,488	4,364
	Exergy		3,595	492	1,292	80		814	1,020
Acrylonitrile (from propane)	Energy		0	3,558	0	31		7,583	5,381
	Exergy		8,703	594	1,269	151		1,097	1,392
Terephthalic Acid	Energy		16	1,465			247	1,985	1,919
	Exergy		332	336			115	487	1,157
Butadiene	Energy			799				712	1,382
	Exergy			324				30	468
Ethylbenzene (Lummus)	Energy		0	1,841				166	1,528
	Exergy		536	687				40	1,082
Propylene	Energy	0	72	1,117				3,376	4,548
	Exergy	851	159	325				310	3,560
p-Xylene	Energy		137	261				462	3,228
	Exergy		246	167				25	1,702
Cumene (SPA)	Energy		0	1,032				834	812
	Exergy		146	370				63	328
Nitric Acid	Energy		66			574		490	232
	Exergy		568			214		47	207

Table 9. Energy and Exergy Losses at the Unit Operation Level (Btu/lb)									
Process		Reactions		Separations				Utilities	
		Endothermic	Exothermic	Distillation	Evaporation	Adsorption/ Absorption	Crystallization	Cooling Water	Heat, Electrical, Steam, etc.
Methanol (Lurgi)	Energy	0	511	1,897		0		1,984	2,273
	Exergy	5	1,762	716		1		262	849
Ammonia	Energy	0	117					1,723	4,596
	Exergy	187	908					133	3,543
MTBE	Energy		261	8,705				8,835	8,868
	Exergy		118	2,522				1,384	2,572
Cumene (Zeolite)	Energy		174	1,019				797	1,061
	Exergy		230	331				120	375
Cumene (AlCl <sub>3</sub> )	Energy		305	922				1,043	1,124
	Exergy		249	365				190	440
Hydrogen	Energy	0	0	6,133		1		14,733	291
	Exergy	871	3,082	1,634		2,448		3,106	283
Vinyl Acetate	Energy		1,249	1,126		143		2,872	2,866
	Exergy		1,114	228		39		513	891
Cyclohexane	Energy		1,064	160				189	465
	Exergy		599	41				21	229
Phenol (from toluene)	Energy		3,021	5,645				1,781	4,787
	Exergy		12,389	1,848				71	2,149
Phenol (from cumene)	Energy		1,698	4,982				5,053	6,942
	Exergy		378	1,275				900	2,016
Sulfuric Acid	Energy		41					378	129
	Exergy		869					18	81
Isobutylene	Energy	0		655				1,231	2,288
	Exergy	93		183				82	518
Aniline	Energy		0	193				1,072	955
	Exergy		1,512	132				149	367
Propylene Oxide	Energy		161	6,917				6,107	7,001
	Exergy		2,429	1,345				397	1,839
Oxygen	Energy			0				203	202
	Exergy			7				1	202
Nitrogen	Energy			0				165	164
	Exergy			3				1	164
Nitrobenzene	Energy		466	146				1,054	1,147
	Exergy		450	37				124	419
Chlorine	Energy	0		7		0		80	11,730
	Exergy	6,070		186		4		0	11,032
Ammonium Nitrate	Energy		0	169				727	171
	Exergy		407	35				150	23
Ethylene (from ethane)	Energy	0	67	0				3,712	9,125
	Exergy	772	48	152				982	6,411

Table 9. Energy and Exergy Losses at the Unit Operation Level (Btu/lb)									
Process		Reactions		Separations				Utilities	
		Endothermic	Exothermic	Distillation	Evaporation	Adsorption/ Absorption	Crystallization	Cooling Water	Heat, Electrical, Steam, etc.
Hydrochloric Acid	Energy		0			435		675	0
	Exergy		435			85		23	0
Methyl Chloride	Energy		0	1,008		0		844	398
	Exergy		237	342		17		73	249
Ethylene Dichloride	Energy		0	583				806	701
	Exergy		630	127				69	168
bisPhenol A	Energy		154	1,415	0	405	57	1,773	2,131
	Exergy		4	405	5	112	3	291	649
Methyl Methacrylate	Energy		1,844	3,105				4,935	3,599
	Exergy		5,949	557				690	7,42
Soda Ash	Energy	0	782	1,000			2	1,450	1,250
	Exergy	41	171	285			35	113	425
Isopropyl Alcohol	Energy		0	3,954				2,765	3,880
	Exergy		3	692				274	808
Urea	Energy		0	431		189		1,614	1,276
	Exergy		40	168		35		137	503
Ethylene Glycol	Energy		0	2,570	2,455			5,025	5,853
	Exergy		368	774	769			979	1,977
Caprolactam	Energy		2,389	2,187			0	4,576	9,521
	Exergy		1,175	729			6	377	2,304
Phosphoric Acid	Energy							417	22
	Exergy							9	10
Ammonium Sulfate	Energy		0	19			5	913	709
	Exergy		127	5			50	147	249
Carbon Black	Energy		0					0	0
	Exergy		4,889					0	0
TOTALS	Energy	0	14,629	86,231	2,455	2,103	311	147,334	165,257
	Exergy	10,222	62,125	27,287	3,335	2,111	209	21,640	76,003



# Recommendations for Research

Energy and exergy analysis of the 53 selected chemical technologies has revealed a number of areas where research and development could have an impact on reducing losses and recovering energy sources. Recommendations for R&D for specific chemical products are described in Table 10, in order of descending recoverable energy potential.

Table 10. Summary of Recommended Research Opportunities for Chemical Products		
Chemical Product	Recoverable Energy (trillion Btu/Yr)	Research Recommendations
Ethylene	261	<p>Large opportunities exist due to high production volume and energy-intensity of current process. Thermal cracking results in a highly reactive product mix that necessitates energy-intensive quenching and complex separation processes. R&amp;D areas that could reduce energy intensity include:</p> <ul style="list-style-type: none"> <li>• Low temperature, more selective retrofit reaction systems to replace pyrolysis and eliminate the need for quenching</li> <li>• Novel separation concepts (perhaps hybrid systems), coupled with new ways of producing ethylene</li> <li>• Dehydrogenation or oxydehydrogenation based on ethane feedstock (dependent on price of NGLs versus petroleum), using novel reactor designs (monoliths, catalytic membranes, microchannel reactors, etc.)</li> <li>• New routes to ethylene based on alternative feedstocks (e.g., ethanol, methanol, methane/syngas, higher olefins), coupled with simpler recovery and purification technologies</li> </ul>
Chlorine	190	<p>An energy efficient alternative to diaphragm electrolytic cells (which dominate U.S. production) already exists in membrane cells. Economics may favor conversion to membrane technology with increasing energy prices.</p> <p>Chlorine is widely used in the chemical industry, but demand in the United States is stagnant. The only growth is in chlorine for producing phosgene, used to make isocyanates, and chlorine for this process is increasingly recovered from the HCl byproduct. Other similar chlorine regeneration schemes are being implemented, as chlorine often functions as an intermediate. Concerns about the hazards of producing, handling, and storing chlorine are also motivating efforts to find processes that do not require chlorine.</p>
Sulfuric Acid	131	<p>This process for producing sulfuric acid from elemental sulfur via sulfur trioxide is an old technology, which has already incorporated many energy recovery and catalyst improvements. There are no obvious opportunities for use of emerging separations technologies.</p>
Ammonia	115	<p>There is little incentive for R&amp;D as the market for ammonia is not growing and producers are under severe economic pressure. A fair amount of energy recovery is already practiced. Improved carbon dioxide removal is one potential area for reducing energy losses.</p>
Hydrogen	110	<p>Hydrogen production is increasing and has many opportunities for R&amp;D:</p> <ul style="list-style-type: none"> <li>• Improved energy recovery in the reformer furnace and reformer gas cooler</li> <li>• Alternatives to reforming, such as partial oxidation of hydrocarbons</li> <li>• New separation methods for recovering hydrogen from industrial waste streams</li> <li>• Production processes with non-fossil fuel feedstocks</li> </ul>

Table 10. Summary of Recommended Research Opportunities for Chemical Products		
Chemical Product	Recoverable Energy (trillion Btu/Yr)	Research Recommendations
Ethylene Oxide	98	<p>Ethylene oxide (EO) technology must operate at low per pass conversion to maintain selectivity and to control the reaction gas composition outside of the flammable region. New process concepts will be needed to lower energy consumption:</p> <ul style="list-style-type: none"> <li>• Fluidized bed reactors</li> <li>• Liquid-phase oxidations, liquid-phase processes using hydroperoxide or hydrogen peroxide</li> <li>• Biooxidation of ethylene</li> <li>• Processes for richer EO-containing streams to reduce large recycle</li> <li>• Novel separations for richer EO streams, including carbonate systems</li> </ul>
Propylene	67	<p>Currently nearly all propylene is produced as a coproduct with ethylene in naphtha crackers. At present there are limited incentives to increase capacity for dedicated production of propylene. However, this could change in future, as the demand for propylene derivatives (polypropylene and propylene oxide) is beginning to outstrip demand for ethylene derivatives.</p>
Terephthalic Acid, purified (PTA)	55	<p>Purification requirements are critical and current yields are approaching stoichiometric. Improvements could be made in purification and catalyst recovery, which are both complex and energy-intensive:</p> <ul style="list-style-type: none"> <li>• Novel separation schemes for solvent recovery and dehydration, and for refining/purifying PTA</li> <li>• Processes requiring less corrosive solvents</li> <li>• Entirely new concepts for producing PTA</li> </ul>
MTBE	53	<p>Demand for MTBE is declining due to legislation banning its use as a gasoline additive. No research is warranted.</p>
Carbon Black	47	<p>Carbon black is mainly used for tire production, a low-growth market, but the production process is very energy intensive (high internal exergy losses) and would benefit from alternative reaction schemes to reduce irreversibilities.</p>
Methanol	36	<p>Expectations for methanol plant construction in the U.S. are not high, unless used as a means for bringing methane to market. Innovations could include:</p> <ul style="list-style-type: none"> <li>• Liquid-phase processes for methanol production</li> <li>• Better process technologies for producing synthesis gas</li> <li>• Improved catalysts, including biocatalysts</li> <li>• Alternative feedstocks (e.g., stranded methane, biomass)</li> <li>• Novel separation technologies to reduce use of distillation</li> </ul>
Acrylonitrile	32	<p>Conversion to acrylonitrile (ACN) takes place at high temperatures and requires the rapid quench of reaction gases and a complex separation scheme (often including refrigeration). Novel ideas are needed to reduce energy intensity:</p> <ul style="list-style-type: none"> <li>• Fluidized beds</li> <li>• Recycle process with substitution of oxygen for air</li> <li>• Biocatalytic production of ACN</li> <li>• Novel concepts for difficult acetonitrile/acrylonitrile separations</li> </ul>
Formaldehyde	31	<p>It is uncertain what the process of choice will be for formaldehyde production (mixed-oxide or silver catalyst). Possible improvements include:</p> <ul style="list-style-type: none"> <li>• More selective, longer-life catalysts</li> <li>• New ways to recover formaldehyde (without polymerization)</li> </ul>

Table 10. Summary of Recommended Research Opportunities for Chemical Products		
Chemical Product	Recoverable Energy (trillion Btu/Yr)	Research Recommendations
Ethylene Dichloride	30	<p>The drive to reduce the amount of chlorinated materials in the environment and the use of PVC may reduce ethylene dichloride demand. Economic and environmental pressures may also increasingly drive production abroad. Nevertheless, there are important opportunities for improving the current process, including:</p> <ul style="list-style-type: none"> <li>• Catalyst improvements to reduce the reaction temperature (thereby reducing irreversibilities) and simplify the process, eliminating quenching of the reactor effluent</li> <li>• Alternatives to the incineration of waste chlorine-containing hydrocarbons, an expensive, noxious, and energy-wasteful step</li> <li>• Improvements to the combined ethylene dichloride and vinyl chloride monomer (VAM) process (almost all ethylene dichloride is used for VAM production)</li> </ul>
Phenol	25	<p>A long-term research goal has been finding a process for producing phenol directly from benzene without co-products. An energy efficient alternative to the dominant cumene oxidation process, which produces acetone as co-product, may become increasingly important if phenol demand continues to grow faster than acetone demand. The current cumene process loses most energy in separation columns, with little opportunity for steam recovery.</p>
Nitric Acid	24	<p>Growth in nitric acid markets is stagnant, with little incentive for R&amp;D. Current processes practice significant heat recovery. Lower temperature catalysts for ammonia oxidation could be an area for research if incentives were present.</p>
Propylene Oxide	20	<p>This process for producing propylene oxide (PO) with co-product tertiary butyl alcohol (TBA) is exothermic, but does not have much opportunity for energy recovery because of low reaction and separation temperatures. Large energy savings could be possible with alternative processes:</p> <ul style="list-style-type: none"> <li>• A process without co-product that could be run economically in small capacity plants (several processes under development use hydrogen peroxide, and are in the process of being commercialized).</li> <li>• An enzymatic process for PO (This has attracted attention in the past, but there is no evidence of current work in this area.)</li> <li>• A biomass-based process for producing polyols, or other PO derivatives (Polyether polyols, used to manufacture flexible and rigid foam, constitute the largest use of PO.)</li> </ul>
Soda Ash	18	<p>This study has analyzed the Solvay process for producing soda ash (sodium carbonate) from sodium chloride, but U.S. producers now recover soda ash from natural deposits of sodium carbonate and sodium bicarbonate or from alkaline brines. These other processes are likely less complicated than the Solvay process, but would involve potentially energy-intensive water removal and calcinations. Soda ash is primarily used for manufacture of glass products, and demand has been stagnant.</p>
Styrene	16	<p>The current high temperature endothermic reaction requires preheating of feed and cooling of effluents with high energy burdens. R&amp;D opportunities to reduce energy use include:</p> <ul style="list-style-type: none"> <li>• Liquid-phase, lower temperature processes with continuous removal of hydrogen</li> <li>• Novel separation technologies to remove hydrogen</li> <li>• Process using diluents other than steam</li> <li>• Alternative feedstock process</li> </ul>
Ethylbenzene	16	<p>Ethylbenzene is used exclusively for the production of styrene, and synergies should be considered, as well as the possibility of finding alternative feedstocks for producing styrene. The current process is relatively efficient; finding more active catalysts to lower the alkylation temperature would be a useful future research area.</p>

Table 10. Summary of Recommended Research Opportunities for Chemical Products		
Chemical Product	Recoverable Energy (trillion Btu/Yr)	Research Recommendations
p-Xylene	15	<p>Considerable energy recovery is already practiced. New opportunities include:</p> <ul style="list-style-type: none"> <li>• New separation technologies, such as removing p-xylene during isomerization</li> <li>• Coupling the p-xylene process with the downstream terephthalic acid process to achieve reductions in energy use (e.g., unique catalyst for oxidation)</li> </ul>
Carbon Dioxide	15	<p>Solvents for recovering carbon dioxide are limited and expensive, and can poison recycle gases. Possible areas for research include:</p> <ul style="list-style-type: none"> <li>• Better solvents, especially adducts that could loosely and reversibly bind with CO<sub>2</sub></li> <li>• Novel separations or hybrid separations with membranes, PSA, etc.</li> </ul>
Vinyl Chloride	14	<p>This process vaporizes ethylene dichloride (EDC), cracks it at high temperatures, and then quenches the reaction gas (to minimize coking). In addition to these energy-intensive operations, many distillation systems are needed to separate the HCl co-product and purify vinyl chloride and EDC. Concepts to reduce reaction temperature and energy for separations include:</p> <ul style="list-style-type: none"> <li>• Cracking additives</li> <li>• Low-temperature catalysts</li> <li>• Alternative feedstocks (e.g., catalytic dehydrogenation of ethyl chloride)</li> <li>• Novel separation systems to reduce distillation</li> </ul>
Ethylene Glycol	14	<p>Ethylene glycol is primarily used for anti-freeze, polyester fibers, and polyester bottles. The last application is a growing rapidly, but ethylene glycol is easily shipped and U.S. producers face strong competition from producers in low energy-cost areas, such as the Middle East. Research opportunities include:</p> <ul style="list-style-type: none"> <li>• Use of non-thermal separations to remove water from the ethylene glycol—perhaps a membrane or hybrid system</li> <li>• Use of renewable biomass feedstocks or biocatalysis (Enzymes may be able to convert ethylene oxide to ethylene glycol at high selectivity and low temperature.)</li> </ul>
Methyl Methacrylate (MMA)	12	<p>Energy savings may be possible in the esterification reactor of this acetone cyanohydrin process. Other processes beginning with isobutylene or tert-butyl alcohol are used internationally, but have not been considered in this study.</p>
Oxygen	7.9	<p>Cryogenic distillation has been highly engineered for efficiency, and is well suited to large-scale production of high purity oxygen and nitrogen. Potential research opportunities include:</p> <ul style="list-style-type: none"> <li>• Membrane separation: Membrane systems have tended to produce low-purity product, and are limited to low volume applications. New materials that achieve higher purity would be of great interest to low-volume users who are not connected to supply pipelines.</li> <li>• Pressure swing adsorption (PSA): PSA has received more attention and success than membranes, and is a newer technology with potential for development (such as improved adsorbents).</li> <li>• Hybrid systems: Increased energy savings may be possible by blending a combination of cryogenic, membrane, and PSA technologies.</li> </ul>
Nitrogen	7.1	<p>Research opportunities for nitrogen are the same as for oxygen.</p>

Table 10. Summary of Recommended Research Opportunities for Chemical Products		
Chemical Product	Recoverable Energy (trillion Btu/Yr)	Research Recommendations
Urea	7.2	<p>Urea plants are almost always co-located with ammonia plants, which provide the ammonia, carbon dioxide, and steam for urea production. The combined process may be more energy efficient than presented here. There is little incentive for developing new processes for urea production, as most new urea plants are built overseas. Nevertheless, two opportunities for development are evident:</p> <ul style="list-style-type: none"> <li>• Eliminate or reduce the amount of ammonium carbamate intermediate that passes through the process and is decomposed to the original feed components</li> <li>• Employ advanced separation processes to replace the complex and energy-intensive decomposition of ammonium carbamate (currently uses two pressure levels of absorption and decomposition)</li> </ul>
Phosphoric Acid	7.1	Phosphoric acid is used mainly for fertilizer production. It has seen little growth, and installed capacity has decreased.
Vinyl Acetate	6.9	<p>Ongoing research for vinyl acetate production includes:</p> <ul style="list-style-type: none"> <li>• Alternative reactor designs, such as a microchannel reactor. BP has commercialized a fluid bed reactor system.</li> <li>• A methanol-based route to vinyl acetate. This would allow production from methane or coal resources instead of petroleum.</li> </ul>
Ammonium Nitrate	6.9	There are few opportunities for energy recovery in this dominant ammonium nitrate process. Several producers have recently closed due to concerns about increased monitoring of ammonium nitrate because of its use in explosives. The primary use of ammonium nitrate is in fertilizers, so substituting other nitrogen-containing species for this application may be a better route for energy savings.
Caprolactam	6.3	All caprolactam is used for producing nylon 6 fibers and resins. There is some growth in the resins market, but the few new plants built have been constructed in Asia. There has been some work on reducing or eliminating production of the ammonium sulfate by-product, but there is little initiative for further research on this process. Other opportunities for research include a more straightforward route to nylon precursors and biomass-derived replacements.
Acetic Acid	6.2	<p>Catalyst research continues to improve acetic acid production. Other needs include:</p> <ul style="list-style-type: none"> <li>• Novel separations to improve carbonylation routes (e.g., separation of gases from carbonylation reaction, and supplementation of distillation)</li> <li>• Other routes to acetic acid (e.g., oxidation of butane, ethylene-based process, or oxidative dehydrogenation of ethane)</li> <li>• Acetic acid from biomass via chemical or biocatalysis</li> </ul>
Hydrochloric Acid	5.9	A novel reactor design that reduces internal irreversibilities recovers some of the energy released by the exothermic reaction. Note that the process studied accounts for less than 10% of hydrochloric acid production.
Cumene	5.1	All cumene goes to production of phenol and acetone. Demand for phenol is not balanced with demand for acetone (which is often sold at distress prices). The result is a major thrust to find alternative processes to produce phenol that do not require propylene or produce acetone. Related research topics include alternative (or one-step) routes to phenol and integration with bisphenol A processes.
Isobutylene	3.8	Most isobutylene is produced as a co-product of olefins; the process analyzed in this study begins with t-butyl alcohol, and is a fairly energy-efficient commercial alternative. Isobutylene can also be produced by dehydrogenation of isobutane, and this process could benefit from new separation technologies, perhaps coupled with process intensification.

Table 10. Summary of Recommended Research Opportunities for Chemical Products		
Chemical Product	Recoverable Energy (trillion Btu/Yr)	Research Recommendations
Aniline	3.4	This exothermic process already incorporates much energy recovery and steam generation. The remaining external exergy losses are low.
Nitrobenzene	2.6	The dominant liquid-phase nitration process runs at low temperatures with little opportunity for energy recovery. Alternative vapor-phase nitration processes using solid catalysts have been reported, and may have more potential for energy efficiency. Almost all U.S. nitrobenzene is used for aniline production, and there may be other more efficient routes to aniline. Aniline is a relatively fast-growing commodity, but most of the growth in demand and capacity is abroad.
Ammonium Sulfate	2.3	There is little incentive for research on this low-temperature, low-energy use ammonium sulfate process. Almost all ammonium sulfate is used for fertilizers, a low-growth market in the United States. The large ammonium sulfate plants are located with caprolactam plants to use waste gypsum from the caprolactam process. New ammonium sulfate capacity will likely be installed with new caprolactam facilities, which are mostly in Asia. Some caprolactam producers are interested in reducing or eliminating ammonium sulfate production; this unlikely event might create an incentive for research on ammonium sulfate.
Butadiene	2.0	Almost all butadiene is present in C <sub>4</sub> streams (butane and derivatives) from refineries and steam crackers, and little dedicated production exists. Improvements could be made in methods of separating butadiene from butane/butene/butadiene mixtures (e.g., new solvents, hybrid systems, membranes, or PSA).
Bisphenol A	1.8	A superior catalytic system to replace hydrochloric acid would simplify the process and eliminate the large energy consumption for HCl recovery (perhaps a strong acid resin catalyst).
Cyclohexane	1.8	The future of cyclohexane production depends on nylon, as almost all cyclohexane is used to produce nylon 6 and nylon 6,6. Nylon intermediates are also produced with a competing phenol processes. Research on cyclohexane production by the hydrogenation of benzene has focused on catalysts for the liquid-phase route. The vapor-phase route analyzed here does not show opportunities for substantial energy savings.
Isopropyl Alcohol	1.5	The process modeled for this study uses a cation exchange resin as catalyst instead of sulfuric acid, which is used in most U.S. plants. The sulfuric acid process is probably more energy intensive, but has not been modeled. Most of the energy losses in this process are to purification columns, with little opportunity for energy savings.
Methyl Chloride	0.9	No significant energy saving potential is apparent. The desire to reduce use of chlorinated materials will likely drive the search for alternatives to chloromethanes.

# References

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- ACC 2005                    *Guide to the Business of Chemistry 2005*, American Chemistry Council, Washington, DC
- ACC 2003                    *Guide to the Business of Chemistry 2003*, American Chemistry Council, Washington, DC
- Ahern 1980                    Ahern, J. E. “The Exergy Method of Energy System Analysis”, John Wiley & Sons, New York, 1980.
- Al-Jarallah, et al. 1988    Al-Jarallah, A. M. and A. K. Lee, “Economics of New MTBE Design”, Hydrocarbon Processing, July 1988.
- ANL 1991                    Argonne National Laboratory, “Energy Conservation Potentials in the Chemical Industry”
- Aspen 2001                    Aspen Technology, Inc. “What is New: Aspen Engineering suite Version 11.1”, October 2001.
- Aspen 2001a                   Aspen Technology, Inc. Aspen Engineering Suite 11.1 Documentation, October 2001.
- C&EN 1996                    Chemical & Engineering News, 6/24/1996
- CMR 2005                    R. Brown, “US Gulf Coast Faces Challenges,” **Chemical Market Reporter**, Vol. 268, No. 6, August 22, 2005 (p 19).
- Cremer 1980                    Cremer, H. “Thermodynamics Balance and Analysis of a Synthesis Gas and Ammonia Plant-Exergy Analysis”. In *Thermodynamics: Second law Analysis*, ed R.A. Gaggioli, ACS Symposium Series 122, American Chemical Society Washington , D.C., 1980, pp111-130.
- EI 2000                        Energy and Environmental Profile of the U.S. Chemical Industry, U.S. Department of Energy, Office of Industrial Technologies, May 2000.
- Gaggioli, et al. 1977        Gaggioli, R.A. and P.J. Petit, “Use the Second Law First,” *Chemtech*, Vol. 7, 1977, pp 496-506.
- Jacob 2001                    Jacobs Engineering Netherlands B.V. “Exercom (Version2) Manual for Aspen Plus Version 10.2, September 2001
- Moran 1982                    Moran, M. J. “Availability Analysis A Guide to Efficient Energy Use” Prentice-Hall, Englewood Cliffs, N.J, 1982
- PEP 2002                    Process Economic Program, SRI International, Menlo Park, California 2002.
- Rosen, et al. 1987            Rosen, M.A. and D.S. Scott, “A Thermodynamic Investigation of a Process for the Production of Ammonia from Natural Gas”. In *Analysis of Energy Systems –Design and Applications*, ed M.J. Moran, S.S. Stecco and G.M.

Reistad, American Society of Mechanical Engineers, New York, 1987, pp 95-100.

Rosen, et al. 1985      Rosen, M.A. and D.S. Scott, “The Enhancement of a Process Simulator for Complete Energy-Exergy Analysis”. In *Analysis of Energy Systems –Design and Operations*, ed. R.A. Gaggioli, American Society of Mechanical Engineers, New York, 1985, pp 71-80.

Shah, et al. 1988      Shah, V. A. and J. McFarland, “Low Cost Ammonia and CO<sub>2</sub> Recovery”, *Hydrocarbon Processing*. 43-46 March 1988.

SRI 1999      SRI PEP Process Module Documentation of 10/18/99, page 2.

SRI 43      SRI PEP Report 43

Szargut, et al. 1988      Szargut, J., D.R. Morris, and F.R. Steward, “Exergy Analysis of Thermal, Chemical and Metallurgical process, Hemisphere Publishing Corp., New York, 1988

Vision 2020      Technology Vision 2020: The US Chemical Industry, American Chemical Society, December 1996.



# Appendix A – Data Table

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Table A1. Energy and Exergy Analysis Results, Btu/lb

Table A1. Energy and Exergy Analysis Results (Btu/lb)

Process	Inputs			Losses			Theoretical Minimum Energy	Ratios *		
	Total Energy (Q <sub>in</sub> )	Total Exergy	Process Exergy (Q <sub>w</sub> )	External Exergy Loss	Internal Exergy Loss	Recoverable Energy (Q <sub>loss</sub> )		Recoverable Energy / Total Energy Input	External Exergy / Total Exergy Input	Internal Exergy Loss / Total Exergy Input
Ethylene (from propane)	8,656	5,534	326	1,806	3,402	5,208	650	60%	33%	61%
Ethylene (from naphtha)	8,139	5,035	217	1,167	3,651	4,818	-989	59%	23%	73%
Ethylene (from ethane)	9,125	6,411	2,998	229	3,184	3,413	1,538	37%	4%	50%
Chlorine	11,730	11,032	3,970	38	7,024	7,062	3,086	60%	0%	64%
Sulfuric Acid	129	81	-1,506	43	1,545	1,588	-2,900	1231%	53%	1907%
Hydrogen	291	283	-33,033	3,742	29,575	33,317	7,391	11449%	1322%	10451%
Ethylene Oxide	7,741	5,735	-6,720	2,096	10,360	12,456	734	161%	37%	181%
Ammonia	4,596	3,543	-351	1,170	2,724	3,894	414	85%	33%	77%
Phenol (from toluene)	4,787	2,149	-12,860	2,357	12,652	15,009	-3,556	314%	110%	589%
Propylene	4,548	3,560	1,440	227	1,892	2,119	846	47%	6%	53%
Terephthalic Acid	1,919	1,157	-4,730	1,440	4,447	5,887	3,047	307%	124%	384%
Acrylonitrile (from propane)	5,381	1,392	-13,152	3,129	11,415	14,544	5,509	270%	225%	820%
Carbon Black	0	0	-12,566	939	11,628	12,567	-803			
Methanol (ICI)	4,883	871	-4,546	1,289	4,128	5,417	802	111%	148%	474%
MTBE	8,868	2,572	-135	1,408	1,299	2,706	124	31%	55%	51%
Methanol (Lurgi)	2,273	849	-4,125	2,165	2,817	4,974	526	219%	255%	332%
Acrylonitrile (from propylene)	4,364	1,020	-8,015	3,191	5,844	9,035	4,355	207%	313%	573%
Ethylene Dichloride	701	168	-971	81	1,058	1,139	-784	162%	48%	630%
Formaldehyde	698	115	-3,209	491	2,833	3,324	802	476%	427%	2463%
Phenol (from cumene)	6,942	2,016	-2,611	1,112	3,515	4,627	-1,470	67%	55%	174%
Nitric Acid	232	207	-1,401	492	1,117	1,609	1,953	694%	238%	540%
Propylene Oxide	7,001	1,839	-2,686	652	3,873	4,525	1,156	65%	35%	211%
Soda Ash	1,250	425	-327	135	616	754	-1,754	60%	32%	145%
Styrene (Fina/Badger)	3,365	1,122	-369	410	1,081	1,491	340	44%	37%	96%
Ethylbenzene (Lummus)	1,528	1,131	-231	601	762	1,363	273	89%	53%	67%
p-Xylene	3,228	1,702	-133	586	1,249	1,835	5	57%	34%	73%
Styrene (Lummus)	4,703	1,697	305	478	914	1,392	340	30%	28%	54%
Ethylbenzene (Mobil/Badger)	1,787	965	-317	870	412	1,282	273	72%	90%	43%
Ethylene Glycol	5,853	1,977	-143	896	1,224	2,120	-415	36%	45%	62%
Vinyl Chloride	2,671	975	147	225	603	828	142	31%	23%	62%
Methyl Methacrylate	3,599	742	-6,067	760	6,041	6,809	-6,359	189%	102%	814%
Carbon Dioxide	2,083	508	-426	289	646	935	N/A	45%	57%	127%
Oxygen	202	202	67	14	121	135	N/A	67%	7%	60%
Urea	1,276	503	-63	137	429	566	-289	44%	27%	85%
Nitrogen	164	164	63	6	96	102	N/A	62%	4%	59%
Phosphoric Acid	22	10	-270	9	270	279	-394	1268%	90%	2700%
Ammonium Nitrate	171	23	-499	152	370	522	-502	305%	661%	1609%
Vinyl Acetate	2,866	891	-1,194	915	1,169	2,084	-1,060	73%	103%	131%
Caprolactam	9,521	2,304	-1,318	355	3,267	3,622	-170	38%	15%	142%

Table A1. Energy and Exergy Analysis Results (Btu/lb)										
Process	Inputs			Losses			Theoretical Minimum Energy	Ratios *		
	Total Energy (Q <sub>in</sub> )	Total Exergy	Process Exergy (Q <sub>w</sub> )	External Exergy Loss	Internal Exergy Loss	Recoverable Energy (Q <sub>loss</sub> )		Recoverable Energy / Total Energy Input	External Exergy / Total Exergy Input	Internal Exergy Loss / Total Exergy Input
Acetic Acid	1,612	786	-512	163	1,134	1,297	436	80%	21%	144%
Hydrochloric Acid	0	0	-530	23	507	530	-1,124			
Cumene (AlCl <sub>3</sub> )	1,124	440	-240	343	337	680	526	60%	78%	77%
Cumene (Zeolite)	1,061	375	-248	304	319	623	526	59%	81%	85%
Cumene (SPA)	812	328	-245	192	382	574	526	71%	59%	116%
Isobutylene	2,288	518	53	314	151	465	54	20%	61%	29%
Aniline	956	368	-1,548	197	1,718	1,915	-2,093	200%	54%	467%
Nitrobenzene	1,147	419	-503	164	758	922	421	80%	39%	181%
Ammonium Sulfate	709	249	-148	106	291	397	-701	56%	43%	117%
Butadiene	1,382	468	55	44	369	413	N/A	30%	9%	79%
bisPhenol A	2,131	649	-290	336	602	938	-491	44%	52%	93%
Cyclohexane	465	229	-543	327	445	772	-499	166%	143%	194%
Isopropyl Alcohol	3,880	808	-124	428	504	932	-50	24%	53%	62%
Methyl Chloride	398	249	-455	139	564	703	-250	177%	56%	227%

- Negative values indicate an exothermic reaction, net chemical conversion exergy inflow

N/A A separation process without chemical reaction

\* Ratios may be higher than 100% because the input energy does not include heat generated by exothermic reactions