Industrial Technologies Program

Chemical Bandwidth Study

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

Summary Report December 2004

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

Preface

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

ITP's Chemicals subprogram supports R&D relevant to the chemical 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.

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Introduction

Overview of Chemical Industry Energy Use

Chemicals manufacture is the second largest energy-consuming enterprise in U.S. industry, accounting for over 6.5 quadrillion Btus (quads) of feedstock and process energy use in 2002, or nearly a third of industrial energy use [ACC 2003]. 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.
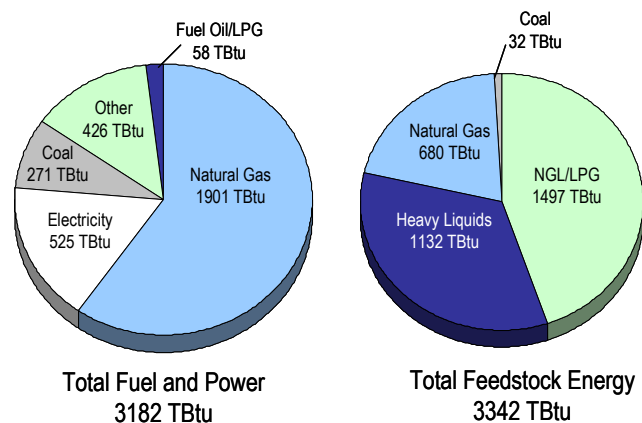
Figure 1. Energy Use in the U.S. Chemical Industry, 2002 [ACC 2003]

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 1990, fuel and power consumed per unit output in the industry has decreased by nearly 40% (see Figure 2). However, as Figure 2 illustrates, efficiency improvements have not been as impressive since the early 1990s, and have remained relatively flat over the last five years. 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 2004].
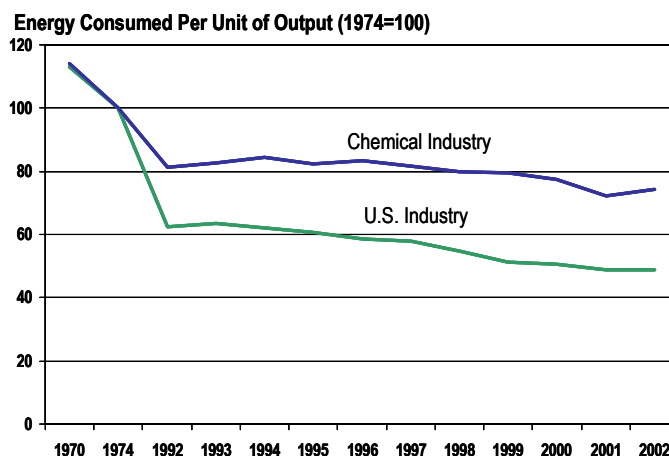
Figure 2. Energy Intensity in U.S. Chemical Industry [ACC 2003]

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; and

- examine energy losses in major unit operations that are common across the chemicals selected.

The 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

Concepts of Energy Bandwidth, Energy and Exergy Analysis

Energy bandwidth analysis provides a snapshot of the energy losses that can potentially be recovered through improvements in technology, process design, operating practices, or other factors. Bandwidth analysis quantifies the differences between these measures:

- theoretical minimum energy (often called asbolute minimum) that is required for a process;

- practical minimum energy that is required for a process, given irreversibilities and other limitations; and

- current energy requirement for an individual process, based on average values in today's manufacturing environment.

The **theoretical minimum energy** is based solely on chemical conversion reactions. It represents the energy required to synthesize the product in its standard state, at 100% selectivity, from the raw materials in their standard states, disregarding irreversibilities. In reality, the energy consumed by a process must exceed the theoretical minimum energy due to the non-standard conditions of reactions, products, and reactants; the formation of by-products; the need to separate products; and other factors. These conditions impose limitations that make it impossible to operate at the theoretical minimum. This higher energy requirement is sometimes referred to as **practical minimum energy**.
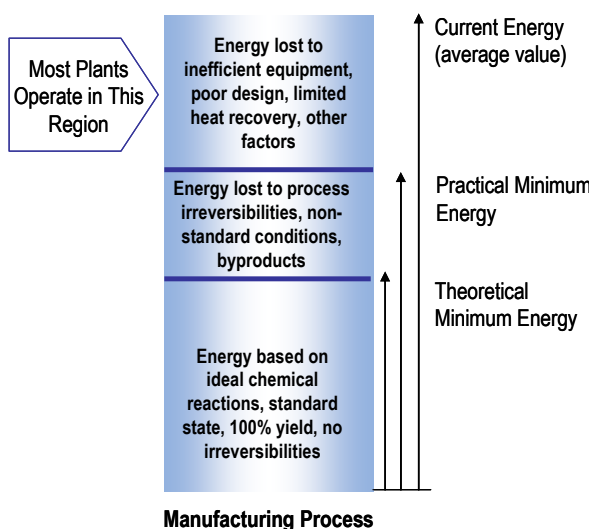
Figure 3. Depiction of Energy Bandwidth

In reality, most chemical processes use significantly more energy than the practical minimum energy requirements due to energy losses. These external energy losses are due to many factors, including inherently inefficient or outdated equipment and process design, inadequate heat recovery, poor integration of heat sources and sinks, poor conversion selectivities, and a host of other site-specific issues. Energy required under actual plant conditions, **current energy**, invariably exceeds the practical minimum because of these external losses.

From an energy efficiency perspective, the difference between current energy and theoretical minimum energy is an important portion of the bandwidth diagram shown in Figure 3. This difference represents the greatest potential target for reduction in energy demand or energy recovery and reuse. However, without examining the quality of the energy in this band, it is difficult to credibly determine how much of that energy it is practical to recover under realistic plant operating conditions. In addition, it is not practical or economically feasible to reduce all process irreversibility-related losses or the inefficiencies. This is where exergy analysis can significantly assist in pinpointing opportunities.

Today engineers and scientists often use enthalpy (a thermodynamic quantity equal to the amount of energy in a system) or energy balances to evaluate the performance of chemical production processes and quantify energy losses. However, this approach does not consider the quality of the energy lost or the

actual energy potential associated with process streams. Using enthalpy, for example, 1,000 Btu/hour of low-pressure steam would compare equally with 1,000 Btu/hour of electricity. In reality, the amount of usable energy from the low-pressure steam is less than a third of that represented by the electricity, because the energy quality of the low-pressure steam is much lower.

Exergy…….

*is defined as the maximum amount of work that can be extracted from a stream as it flows toward equilibrium. This follows the 2nd 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**.*

Exergy analysis provides a powerful tool for assessing the quality of energy and quantifying the portion of energy that can be practically recovered. Exergy analysis uses parameters such as temperature or pressure to determine energy quality and calculate potentially recoverable energy. Exergy, or energy quality, diminishes each time energy is used in a process. For example, a large percentage of energy content can be extracted from flowing steam at high temperatures. As the steam temperature drops (e.g., after passing through a heat exchanger), the percentage of energy that can be recovered is reduced. This drop in energy quality is referred to as a loss of exergy or energy degradation.

Figure 4 illustrates the change in energy quality with temperature drop. At 110°F, little recoverable energy (exergy) is available when compared with the same stream available at higher temperatures. Exergy analysis also quantifies energy that cannot practically be recovered and accounts for non-standard conditions and irreversibilities. It does not, however, take into account the economic feasibility of energy recovery.

The concept of exergy and energy quality as applied to a chemical process is depicted in Figure 5. Total energy input (Q_{IN}) is comprised of both exergy and non-exergy input. During the process, total energy input is converted to some useful work (Q_{W}), while some is lost due to internal and external energy loss factors (Q_{LOSS}). The non-exergy component of total input energy has zero quality and is rejected (Q_{REJECT}). It is assumed that it is technically feasible to recover some portion of Q_{LOSS} (the exergy component).

Figure 4. Exergies of a Stream Containing 10 Btu/hr at Variable Temperatures

Q_W=*Useful Process Work*

Q_{IN}=*Total Energy Input (Exergy + Non-Exergy Input)* → **PROCESS** → Q_{REJECT}=*Zero Quality Energy (Unrecoverable Energy/ Non-Exergy Input)*

Q_{LOSS}=*Non-Product Effluents (external exergy loss) + Process Irreversibilities (internal exergy loss) (Recoverable Energy)*

$Q_{IN} = Q_W + Q_{LOSS}$ *(exergy component)* $+ Q_{REJECT}$ *(non-exergy component)*

Figure 5. Concept of Exergy in a Chemical Process

Figure 6. Concept of Exergy, Theoretical Minimum, and Actual Process Energy

External exergy losses are embodied in non-product effluents such as vent gases, byproducts and waste water. Internal exergy losses are due to process irreversibilities. Energy quality is the ratio of exergy content to energy content. For this analysis, streams with a quality greater than 20% were assumed to be economically recoverable; between 5-20% some energy might be economically recoverable; below 5% energy recovery might not be likely.

Figure 6 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.

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 the list of top 100 chemicals published by the American Chemistry Council [ACC 2003]. The technologies selected for study are necessary 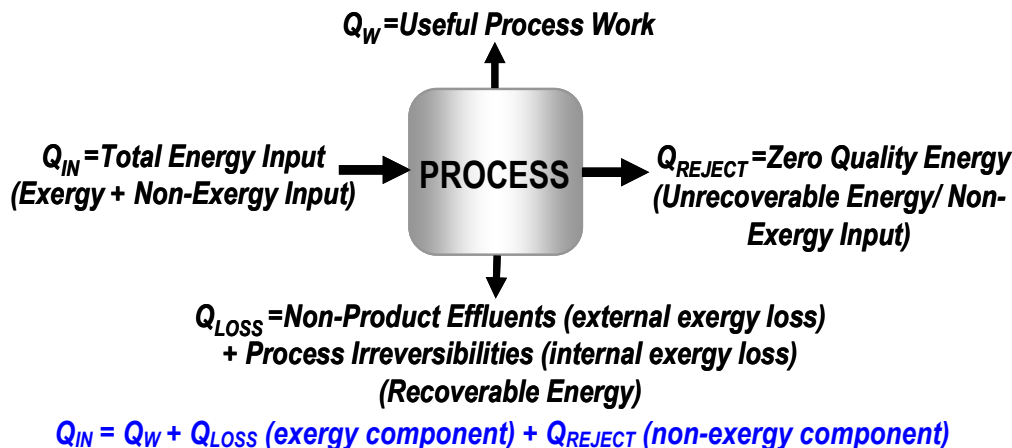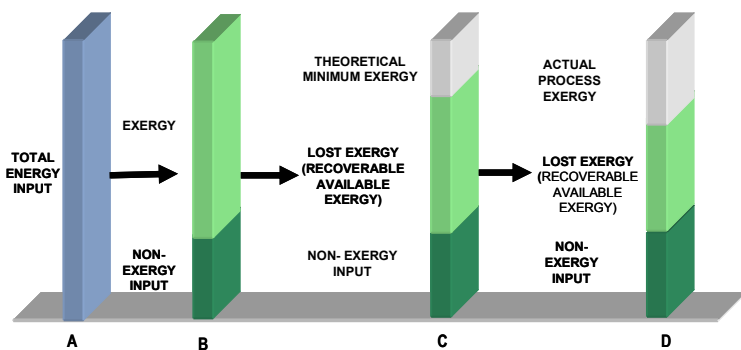to the manufacture of 18 major chemical products representing about 30% of the production volume of the top 50 chemicals, as shown in Table 1. These 18 chemical products also represent more than half of the organic chemicals in the top 50 list, and about 11% of the inorganic chemicals listed among the top 50.

The process energy use shown in Table 1 was estimated for each chemical based on current production and total energy input values (Btu/lb) used in the analysis. Energy represented by the manufacture of these chemicals accounts for nearly 40% of 2002 energy consumed for fuels and power [ACC 2003]. Analysis was performed on 25 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 six of the chemicals studied.

Energy and Exergy Modeling Methodology

Model Integration

To calculate recoverable energy, the basic concepts of energy and exergy described previously were applied to the selected chemical processes shown in Table 1 using three tools:

- process flow sheets and stream properties developed in AspenTech's Aspen Plus model 11.1;
- 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.

Table 1. Chemicals Selected for Energy and Exergy Analysis				
Chemical	U.S 2002 Production, Top 125 Chemicals (billion lbs)	Estimated Process Energy (TBtu)	% of Top 50 Chemicals	% of Organics in Top 50 Chemicals
Ethylene	52.1	437.4	5.9	13.3
Propylene	31.8	144.7	3.6	8.1
Ammonia	29.0	133.5	3.3	na
MTBE	19.8	175.6	2.3	5
Vinyl Chloride	17.3	46.2	2	4.4
Carbon Dioxide	15.5	32.3	1.8	3.9
Nitric Acid	14.9	3.5	1.7	na
Ethylbenzene	11.9	19.8	1.4	3
Styrene	11.0	44.2	1.3	2.8
Terephthalic Acid	9.4	18	1.1	2.4
Formaldehyde	9.3	6.5	1.1	2.4
P-Xylene	8.3	26.8	0.9	2.1
Ethylene Oxide	7.9	56.6	0.8	1.9
Cumene	7.7	11.5	0.9	2
Methanol	7.3	25.9	0.8	1.8
Acetic Acid	4.8	7.7	0.5	1.2
Butadiene	4.1	5.7	0.5	1
Acrylonitrile	2.7	13.1	0.3	0.7
TOTALS	264.8	1209.0	30.2%	56.0%

A schematic of the modeling approach is shown in Figure 7. Process modeling was first accomplished using the Aspen Plus model, drawing on process modules available from the SRI Consulting/Aspen Process Economics Program (PEP) library. This library utilizes information from public sources and in-house engineering expertise to reproduce the technology of a particular licensor, plant operator, or research organization. Currently this library only contains 15 technologies from the list of top 50 chemicals, although more are expected to be added. Processes for which AspenPlus models were not available from the SRI PEP library were developed using data from open literature sources. The ApsenPlus models provide the process energy and material balances for the selected chemical manufacturing processes.

AspenPEP Library
Database of SRI process models built into AspenPlus flowsheet models

AspenTech AspenPlus 11.1 version

Steady-State Process Models

Process Modeling

ExerCom (Jacobs Engineering)

Energy/Exergy of Streams

Psage-Developed Software

Energy/Exergy of Process Units
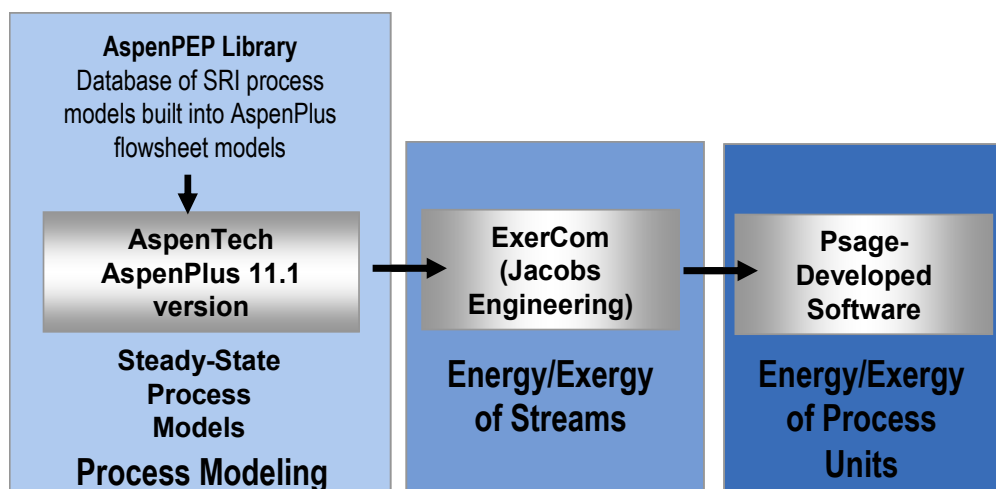
Figure 7. Integrated Modeling Approach Used for Exergy and Energy Analysis

Table 2. Chemical Technologies Selected for Analysis	
Chemical	**Process Technologies Analyzed**
Ethylene	Braun – conventional cracking of propane with front-end de-ethanization M.W. Kellogg – millisecond cracking of naphtha with front-end de-methanization
Propylene	Fina Research – propylene from hydrotreated cracked naphtha using a de-aluminated silicalite catalyst (ZSM-5) with a silica binder
Ammonia	Derived from Szargut and Cremer (see references) – ammonia from reforming of methane
MTBE	Derived from Al-Jarallah et al (see references) – MTBE from reaction of methanol and isobutylene using a sulfuric acid catalyst
Vinyl Chloride	Hoechst – vinyl chloride from ethylene dichloride using gas phase de-hydrochlorination
Carbon Dioxide	DOW – absorption of carbon dioxide from gas power plant sulfur-free flue gas with mono-ethanolamine
Nitric Acid	Derived from Szargut (see references) – nitric acid produced by oxidizing ammonia with air on a platinum/rhodium alloy catalyst
Ethylbenzene	Lummus Crest/Unocal/UOP – ethylbenzene from liquid phase benzene alkylation Mobil/Badger – ethylbenzene from vapor phase benzene/ethylene alkylation
Styrene	Lummus Crest – styrene from ethylbenzene via zeolite-based liquid phase dehydrogenation Fina/Badger – styrene from ethylbenzene via vapor phase dehydrogenation
Terephthalic Acid	Amoco – terephthalic acid produced by oxidizing p-xylene in the presence of cobalt-manganese-bromine catalyst (liquid phase)
Formaldehyde	BASF – formaldehyde from methanol using a silver catalyst
P-Xylene	Para-xylene produced from a mixture of C8 aromatic isomers (p-xylene, o-xylene, m-xylene, ethylbenzene) via front-end isomerization and fractionation (generic)
Ethylene Oxide	Shell/Union Carbide – ethylene oxide by direct oxidation of ethylene with oxygen
Cumene	UOP – solid phosphoric acid (SPA)-catalyzed reaction of benzene/propylene feed Zeolite – Cumene from propylene alkylation of benzene using zeolite catalyst (similar to Mobil/Badger, UOP and DOW-Kellogg zeolite processes) $AlCl_3$-catalyzed – cumene from propylene alkylation of benzene using $AlCl_3$ catalyst (similar to Monsanto-Kellogg zeolite process)
Methanol	ICI LP – methanol from natural gas using low-pressure reforming with a nickel-based catalyst in the reformer and a copper catalyst for methanol synthesis Lurgi – methanol from a two-stage combined reforming process
Acetic Acid	Chiyoda/UOP – acetic acid via low-pressure methanol carbonylation using rhodium catalyst and methyl iodide as a promoter
Butadiene	Nippon Zeon – butadiene recovered as a byproduct from steam cracking of liquid feedstocks (C5s, C6s, C7s, C8s)
Acrylonitrile	SOHIO/BP – acrylonitrile via ammoxidation of propylene (ammonia and propylene) using a metal complex catalyst based on bismuth molybdate SOHIO/BP – acrylonitrile via ammoxidation of propane in a fluidized bed reactor using a metal catalyst complex of vanadium, tin and tungsten

As shown in Figure 7, after process models are developed the ExerCom model uses the output of the Aspen Plus simulation and 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 that some data be calculated 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 computer program interfaces directly with the AspenPlus and ExerCom results to calculate the exergies of heat, work, and solid streams around individual process units and for the overall process model. Exergies of heat streams not calculated by ExerCom are computed from enthalpies using the Carnot quality factor (η_c). Where model boundaries do

not include all exergy inflows (mainly refrigeration and separation units), values must be estimated based on known exergetic efficiencies of similar unit operations.

Unit Processes and Equipment

A number of assumptions were necessary to calculate the energy and exergy losses possible from the 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.

Table 3. Energy and Exergy Assumptions for Process Equipment Models	
Process Unit	**Description**
Reactors (exothermic)	Reactor in which the heat of reaction is removed by some combination of sensible heat in streams leaving the reactor or in generated steam used elsewhere in the plant (ordinarily no external exergy loss). Internal exergy losses, however, can be substantial (generally irreversibilities created by mixing of streams of very different temperatures and compositions and by heat transfer across larger temperature differences).
Reactors (endothermic)	Reactor in which feed streams supply all of the energy absorbed in the reaction, with the exception of furnace reactors, such as reformers (no external exergy losses). Internal exergy losses are considerable because feed streams are much hotter than reactor effluents.
Distillation Columns	Columns in which chemicals are separated by boiling point differences. 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 differences among temperature and composition of feed, overheads, and bottoms.
Heat Exchangers	Two configurations are possible: (1) process streams on both sides, or (2) process stream on one side with heating and cooling medium on the other side. For (1), exchangers will have no external exergy loss, and internal exergy loss will depend on temperature difference between heated and cooled media. For (2), external exergy loss relates to the quality of the energy loss. A low exergy loss, for example, would suggest little opportunity for energy recovery.
Process Furnaces	Variety of furnaces used to superheat steam, heat process streams, or enable chemical reactions (reformers). All are modeled with no energy loss or external exergy loss as the fuel is accounted for separately and the stack gases are not included in the analyses when the fuel is not included as a stream. Large internal exergy losses are typical due to large changes in process stream temperatures and large driving forces for heat transfer.
Compressors and Expanders	Energy and external exergy losses result from intercoolers. Internal exergy losses depend upon differences in temperature and pressure between inlet and outlet gas streams and assumed efficiencies for pumps or compressors.
Pumps	Not all pumps are included in the flowsheets. When they are indicated, they contribute little to no measurable exergy or energy losses.
Drums/Tanks	Energy and exergy losses only occur when a heater or cooler is present in the system. In flash drums, internal exergy losses are due to changes in pressure, state and composition from inlet stream to outlet streams. For receivers with multiple inlets and one outlet stream, internal exergy changes are due to temperature differences and composition changes of streams. Knockout drums or other units have modest internal exergy changes.
Mixers/Splitters	Essentially artifacts of the model (simulating mixing or splitting of streams) and do not contribute to the exergy analysis.
Other Equipment	PSA (pressure swing absorption) units, multi-effect evaporators, other separators. These are modeled as black box units in some cases. Not all have energy and 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>
<tr><th colspan="2">Table 4. Model Outputs</th></tr>
<tr><td>

Total Process Energy Input (Q_{In}) – *all energy inputs to the process regardless of quality*

Total Process Exergy input (TPEI) – *the component of input energy that can be converted to work or recovered*

Actual Process Exergy (Q_W) – *the component of input exergy that is converted to useful work*

Theoretical Minimum Process Energy (TMPE) – *the minimum amount of energy required for the process based on chemical reactions and ideal or standard conditions and 100% yield*

External Exergy Loss (EEL) – *potentially recoverable energy in the form of non-product effluents such as steam and wastewater*

Internal Exergy Loss (IEL) – *potentially recoverable energy lost throughf process irreversibilities*

Potentially Recoverable Available Energy (Q_{Loss}) – *the sum of recoverable energies (IEL and EEL)*

</td></tr>
</table>

A sample output of the analysis is provided in Figure 8 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 source of energy and exergy losses were due to vaporizing ethylene dichloride, the endothermic furnace reactor (rapid quench), low temperature distillations, and separation of hydrochloric acid (HCl).

Chemical reactions can be either endothermic (heat absorbing) or exothermic (heat generating). For endothermic reactions, the energy converted to useful work (Q_W) will be shown with an arrow flowing away, indicating that it was absorbed by the process. For exothermic reactions, Q_W will be shown with an arrow flowing toward the process, indicating additional heat energy has been generated. Figure 8 is an example of an endothermic process.

The modeling outputs for each of the chemical technologies selected can be evaluated in various ways 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.

Q_W, Useful Work= **147**
(Chemical Conversion)

■ Energy
■ Exergy

Q_{IN} Input = **2,671**
= **975**

PROCESS

Q_{REJECT} = **1,696**

Irreversibility = **603**
(Internal Exergy Losses)

Effluents = **225**
(External Exergy Losses)

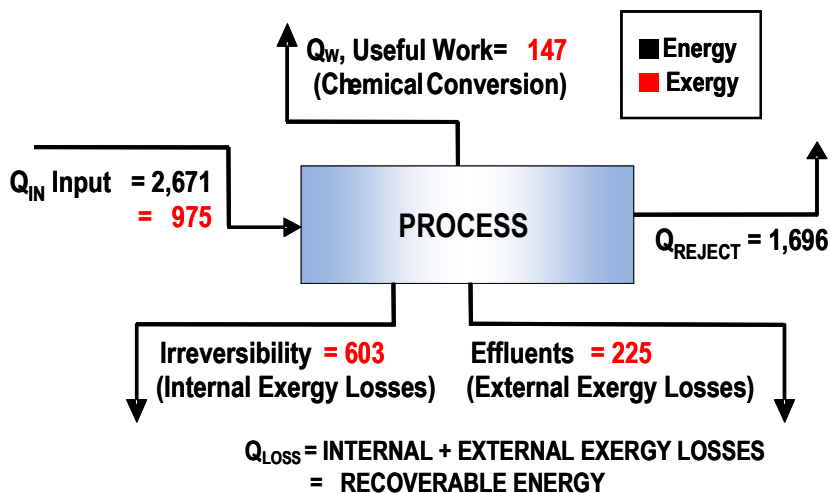Q_{LOSS} = INTERNAL + EXTERNAL EXERGY LOSSES
= RECOVERABLE ENERGY

Figure 8 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 for the following reasons:

- kinetic data and proprietary process data are not always available;
- 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. However, the quality factor inherently takes into consideration that low quality energy is probably not economically suitable for recovery and uses this as a measure of recoverable energy.

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

An energy and exergy diagram similar to that shown in Figure 8 was developed for all 25 of the process technologies studied, including multiple technologies for some products. The results of this analysis are shown in Table 5.

There is great potential for energy recovery in the chemical processes analyzed. The total potentially recoverable energy identified for the 25 processes studied is nearly 900 trillion Btus (using average values for multiple technologies when applicable). Recoverable energy is assumed to be of high enough quality to warrant recovery, regardless of economic feasibility.

| Table 5. Energy and Exergy Analysis Results for 25 Chemical Technologies (Btu/lb)							
Process	Total Energy Input Q_{IN}	Process Exergy Input	Actual Process Exergy Q_W	Theoretical Minimum Energy	Recoverable Energy Q_{LOSS}	Ratio of Q_{LOSS}/Q_{IN} *	Recoverable Energy (TBtu/yr)
Ethylene (Braun)	8,656	5,534	326	650	5,208	60%	271.3
Ethylene (Kellogg)	8,139	5,035	217	650	4,818	59%	251
Ammonia	4,596	3,543	-351	414	3,967	86%	115.0
Ethylene Oxide	7,741	5,735	-6,720	734	12,456	161%	98
Propylene	4,548	3,047	1,440	846	2,119	47%	67.4
Terephthalic Acid	1,919	1,157	4,730	3,047	5,887	307%	55.3
MTBE	8,868	2,572	-135	124	2,706	31%	53.6
Methanol (ICI LP)	4,883	871	-4,546	802	5,417	111%	39.5
ACN From Propane	5,381	1,392	-13,152	5,509	14,544	270%	39.3
Methanol (Lurgi)	2,273	841	-4,132	802	4,974	219%	36.3
Formaldehyde	698	115	-3,209	802	3,324	476%	30.9
ACN From Propylene	4,364	1,020	-8,015	4,355	9,035	207%	24.4
Nitric Acid	232	207	-1,401	1,953	1,609	694%	24.0
Styrene (Fina/Badger)	3,365	1,122	369	340	1,491	44%	16.4
Ethylbenzene (Lummus)	1,528	1,147	-231	273	1,363	89%	16.2
Styrene (Lummus)	4,703	1,697	305	340	1,392	30%	15.3
Ethylbenzene (Mobil/Badger)	1,787	965	-236	273	1,282	72%	15.3
p-Xylene (Isomerization)	3,228	1,702	-133	5	1,835	57%	15.2
Carbon Dioxide	2,083	508	-426	N/A	935	45%	14.5
Vinyl Chloride	2,671	975	147	142	828	31%	14.3
Acetic Acid	1,612	786	-512	436	1,297	80%	6.2
Cumene (AlCl₃ Cat.)	1,124	440	-240	526	680	61%	5.2
Cumene (Zeolite Cat)	1,061	375	-248	526	623	59%	4.8
Cumene (SPA Cat)	812	328	-245	526	574	71%	4.4
Butadiene	1,382	468	55	N/A	413	30%	1.7

-        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.
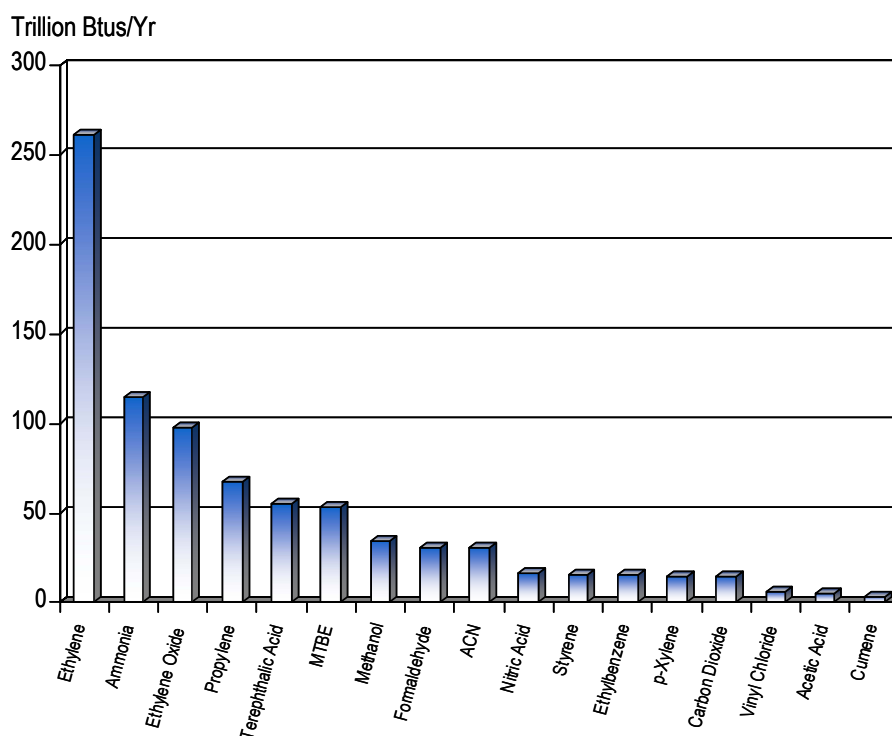
Figure 9. Comparison of Recoverable Energy Across Chemical Technologies

A comparison of the recovery energy potential for each chemical product is shown in Figure 9, in descending order. Where multiple technologies were evaluated the average values for recoverable energy were used. Ethylene, ammonia, ethylene oxide, propylene, terephthalic acid and MTBE exhibit the largest potentials for energy recovery in terms of trillion Btus.

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 has 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.

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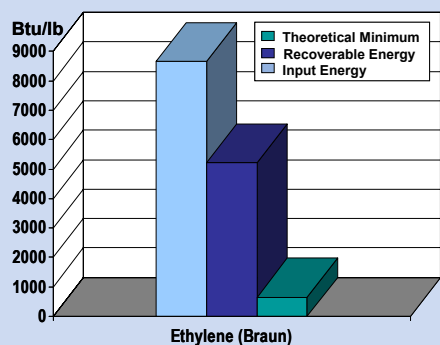
Ethylene from Propane (Braun) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Cracking And Quenching	425	6	38	1046	1084	21
Compression And Deacidification	1879	27	208	590	798	15
Deethanization	1294	18	231	65	296	6
Demethanization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

Cracking of Naphtha – 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 Braun process, the highest energy-exergy consumption is concentrated in the front end of the process. The Kellogg process is more exothermic, and requires less input process energy but exergy losses are double in cracking and quenching due to the higher compression ratio used (525 psia versus 140 psia for Braun). Total process energy required is about 12 times greater than the theoretical minimum. Substantial losses occur in the demethanizer column due to the condenser, where the coolant is ethylene refrigerant. Another significant source of losses is cracking and quenching, mostly due to the cracking furnaces and the large towers where temperature differences create exergy losses. The cracked gas compressor interstage coolers are large sources of losses.
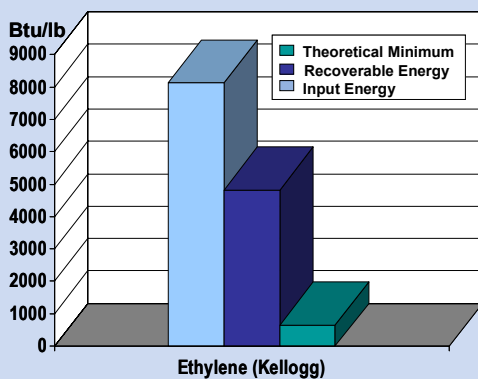
Ethylene from Naphtha/Gas Oil (Kellogg) Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Cracking And Quenching	1851	24	183	1678	1861	39
Compression And Deacidification	2958	38	208	540	748	16
Demethanization	1712	22	614	359	974	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
TOTALS	7807		1167	3651	4818	

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 is the largest source of energy-exergy losses (hot exit carbon dioxide stream, exchanger cooling of MEA). 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.
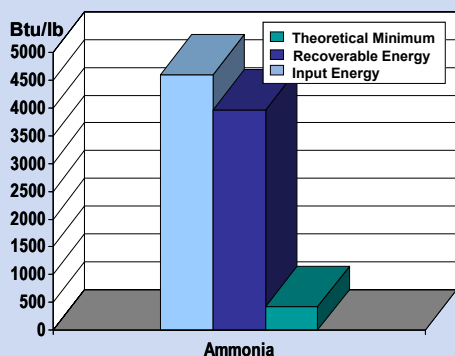
Ammonia from Natural Gas Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Preheating/Reforming	556	10	206	1272	1478	38
Shift	0	0	0	164	164	4
Gas Upgrading	2608	49	614	182	796	20
Ammonia Synthesis	1897	36	269	1081	1350	35
Heat Recovery	263	5	81	25	106	3
TOTALS	5324		1170	2724	3893	

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 too low a temperature 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 (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 area due to large temperature differentials between the inlet gas and exothermic conditions in the reactor.
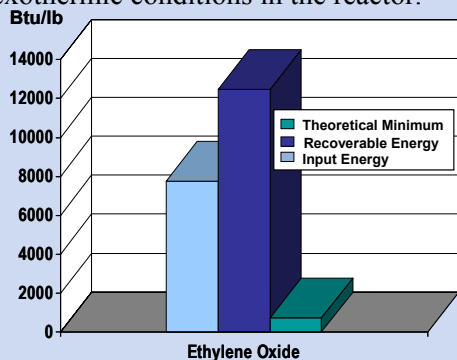
Ethylene Oxide (Shell) Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Feed Pre-Heat	252	2	28	1010	1039	8
Reactor	0	0	0	4163	4163	33
EO Absorber	0	0	0	885	885	7
EO Stripper	985	7	277	3705	3982	32
EO Purification	12352	91	1792	596	2388	19
TOTALS	13588		2096	10360	12456	

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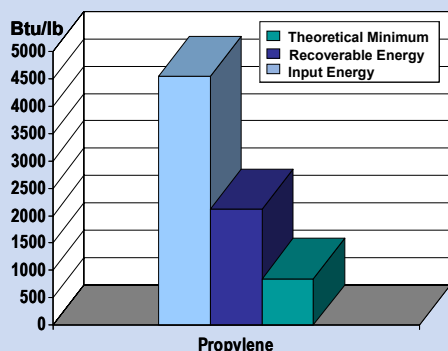
Propylene from Naphtha Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Reactor	133	7	21	1513	1534	72
Product separation	1318	74	191	292	482	23
Product purification	293	16	15	22	37	2
By-products	41	2	1	66	67	3
TOTALS	**1786**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

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. Total process energy input is about twice that of theoretical minimum energy requirements. 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 feed streams and the 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.
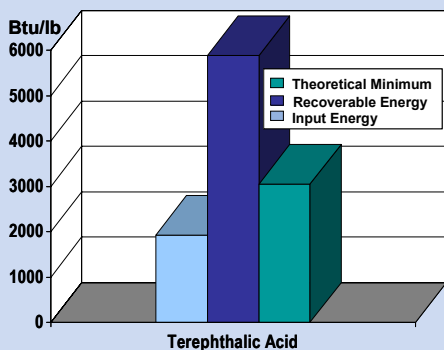
Terephthalic Acid from p-Xylene Oxidation Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Oxidation	1943	36	657	3635	4292	73
CTA Crystallizer	1766	33	288	273	561	10
Hydrogenation	49	1	11	435	446	8
PTA Purification	1616	30	484	104	588	10
TOTALS	**5374**		**1440**	**4447**	**5887**	

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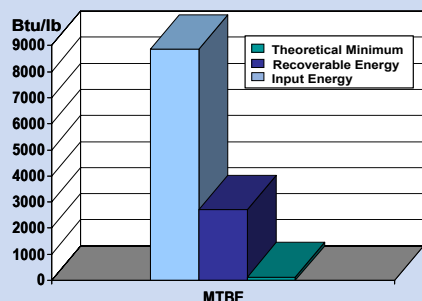
MTBE Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Reactor	297	3	26	137	163	6
Methanol Recovery	63	1	9	7	16	1
MTBE Recovery	8744	96	1373	1155	2527	93
TOTALS	1786		227	1892	2119	

Formaldehyde

This exothermic process produces formaldehyde from methanol using a silver-based catalyst, and is based on BASF technology. Total process energy input is about 4 times greater than theoretical minimum energy requirements. 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.
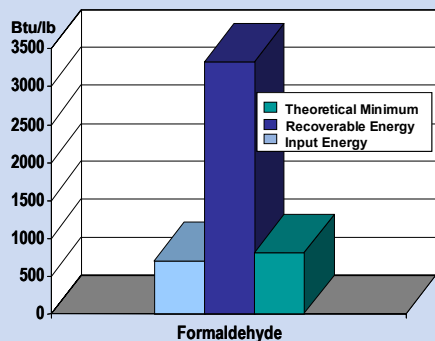
Formaldehyde from Methanol Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Feed Air/Recycle Air Mixer	0	0	0	19	19	0.56
Feed Air Compressor	0	0.00	0	17	17	0.51
Feed Heater	0	0.00	0	97	97	2.91
Reactor	2268	94.8	487	2463	2950	88.9
Absorber	0	0.00	0	235	235	7.07
Recycle Air Purge	124	5.20	4	2	6	0.19
TOTALS	2392		491	2833	3324	

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 that of the theoretical minimum energy required. The sources of large exergy losses in the refining section are a primary distillation column and large heat exchanger. The reforming furnace experiences large internal exergy losses primarily due to large differences in the temperatures of inlet and effluent streams and combustion gases.
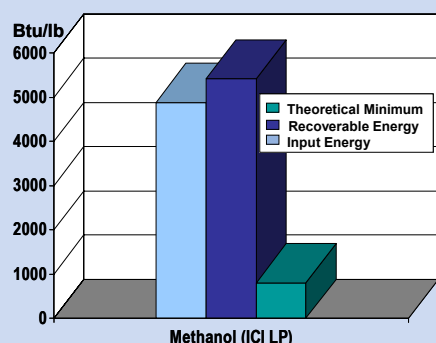
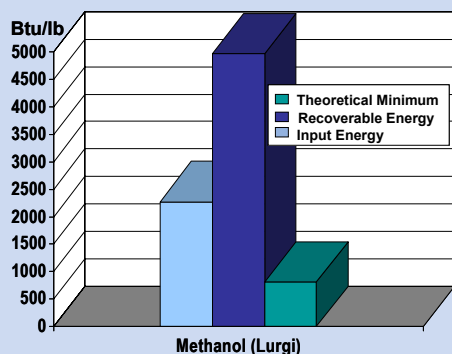| Methanol from Natural Gas (ICI LP) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Reforming section	176	2	8	2,791	2,799	52
Synthesis section	313	3	47	516	562	10
Refining section	9,391	95	1,234	822	2,056	38
TOTALS	**9880**		**1289**	**4128**	**5416**	

LurgiTechnology – 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. Preheating the feed within the reactor system is the source of large internal exergy losses in the synthesis section due to large temperature differences.

Methanol from Natural Gas (Lurgi) Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss 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
TOTALS	**7594**		**2165**	**2816**	**4982**	

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 steams 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 the HCN stripper column and condenser, which is cooled with refrigeration and is very energy-intensive.
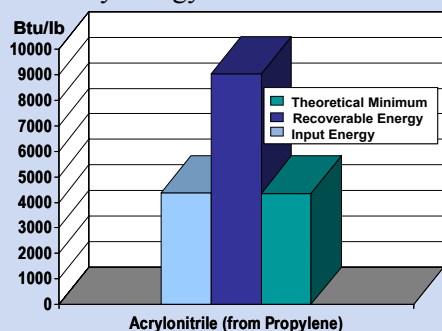
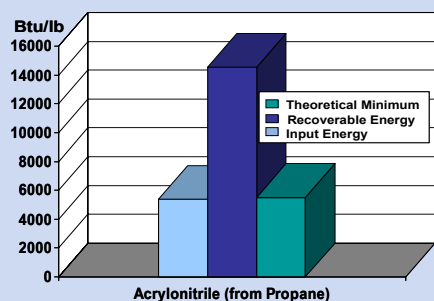| Acrylonitrile by Propylene Ammoxidation (SOHIO-BP) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Propylene Ammoxidation	3624	24	354	4238	4592	51
Acrylonitrile Separation	4729	31	404	1599	2003	22
Heat & Refrigeration Recovery	6727	45	2435	5	2440	27
TOTALS	**15081**		**3193**	**5842**	**9035**	

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 required (considerable energy is produced by the exothermic reaction). It is similar to the propylene ammoxidation process although reaction system performance is different, leading to changes in downstream processing. Differences in energy and exergy input and losses are related to differences in feedstock, products and byproduct yields. Energy losses are similar to those of the process above. The propane process input energy is not only higher than that for propylene, but the quality of input energy (exergy/energy) is also higher. The higher selectivity of the propylene process leads to lower exergy losses in production, separation and cooling of fewer byproducts. The propane process requires more energy for compression and byproduct separation. Being more exothermic, the propane process also offers more opportunity for steam generation, but is subject to more process irreversibilities due to conversion at higher temperatures. A key difference is in the ammoxidation reactors, where internal exergy losses of the process are almost double. 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 Energy 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
TOTALS	**14823**		**3129**	**11415**	**14544**	

Styrene

Lummus/Monsanto/UOP – This process is based on production of styrene via adiabatic dehydrogenation of ethylbenzene, an endothermic reaction. 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 at lower temperatures. Another source of losses is the steam superheater. Other losses are found in strippers and fractionators and are due primarily to large temperature differences leading to process irreversibilities.
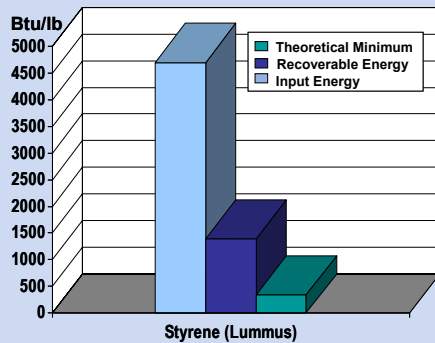
Styrene (Lummus/Monsanto/UOP) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Steam Compressor	17	0	17	11	28	2
Steam Super heater	0	0	0	193	193	14
Feed- Preheat/Reactor	0	0	0	371	371	27
Air Coolers	3597	84	408	142	550	39
Condensate 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
TOTALS	**4286**		**478**	**914**	**1392**	

Styrene (Fina/Badger) – This endothermic process is very similar to the Lummus process, except for modest differences in the reactor section. 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, although the quality of the energy lost is relatively low. The feed preheat is the source of significant exergy losses due to high 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, and the large condenser load is removed with cooling water at too low a temperature 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.
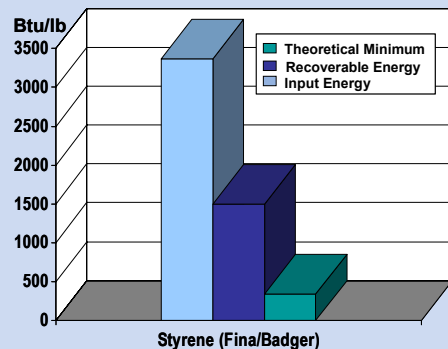
Styrene (Fina/Badger) Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Steam Compressor	1	0	1	0	1	0
Steam Super heater	0	0	0	29	29	2
Feed- Preheat/Reactor	0	0	0	759	759	51
Air Coolers	2716	51	158	48	206	14
Condensate Recovery	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
TOTALS	**5293**		**410**	**1081**	**1491**	

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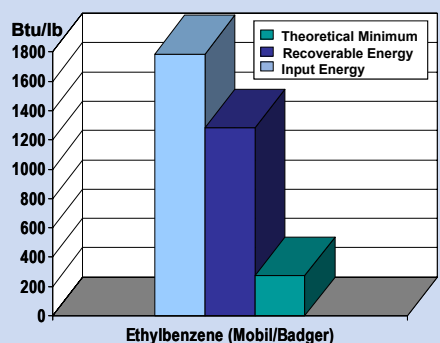
Ethylbenzene (Mobil/Badger) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Benzene Fractionator	1850	82	757	267	1024	80
Primary Reactor	0	0	0	108	108	8
Ethylbenzene Fractionator	331	15	92	17	108	8
Poly Ethylbenzene Fractionator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

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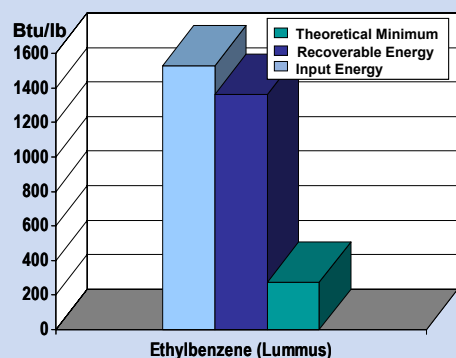
Ethylbenzene (Lummus) Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Benzene Fractionator	1654	82	501	132	633	46
Primary Reactor	0	0	0	542	542	40
Ethylbenzene Fractionator	344	17	96	13	110	8
Poly Ethylbenzene Fractionator	10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

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 made possible by 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, which performs the absorption of nitrogen dioxide in water while reacting it to 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).
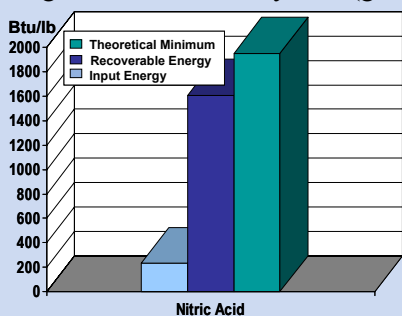
Nitric Acid via Ammonia Oxidation Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Reaction	442	20	73	869	942	59
Product Separation	689	31	10	227	237	15
Heat Recovery	1,100	49	409	20	430	27
TOTALS	**2230**		**492**	**1117**	**1608**	

p-Xylene

This process is based on conventional technology where p-xylene is produced from a mixture of C8 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 due 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.
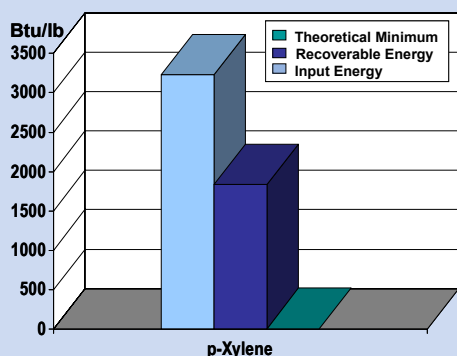
p-Xylene from C8 Isomers Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Isomerization	1470	56	288	989	1277	70
Fractionation	1165	44	298	260	558	30
TOTALS	**2635**		**586**	**1249**	**1835**	

Carbon Dioxide

Carbon dioxide is produced by recovery from gas streams where it is a contaminant or byproduct. The majority comes from ammonia, hydrogen or ethylene oxide producing plants. The total process input energy is about 19 times greater than the theoretical minimum energy required. The most common process is absorption via a physical or chemical solvent. This analysis models a process where monoethanoalamine (MEA) to recover carbon dioxide from power plant flue gas. 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 could be possible from the associated cooling water recycle, make-up and purge loop.
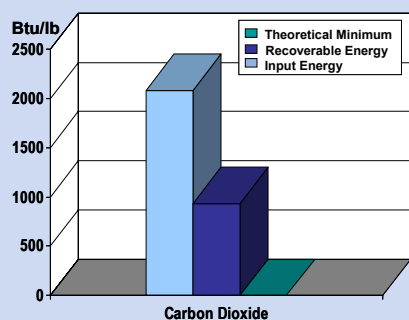
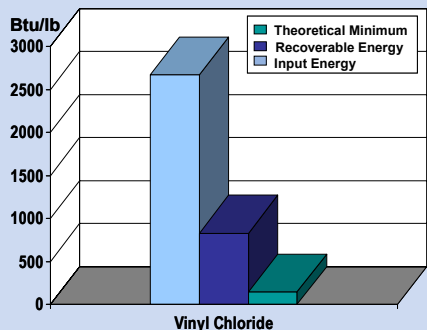| Carbon Dioxide Recovery with MEA Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
CO2 Absorber	377	12	8	478	486	52
Mea-Makeup Mixer	0	0	0	9	9	1
Lean MEA Cooling Exchanger	649	21	58	1	59	6
Rich MEA Solution Pump	0	0	0	0	0	0
Rich/Lean Mea Solution Exchanger	0	0	0	24	24	3
CO2 Stripper	1001	33	171	42	213	23
Feed Quencher Column	0	0	0	40	40	4
Quench/Makeup Water Mixer/Splitter	589	19	24	17	41	4
Lean Mea/Makeup Water Mixer	94	3	12	33	45	5
Quenching Water Cooling Exchanger	336	11	17	1	18	2
TOTALS	**3045**		**289**	**646**	**935**	

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 Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss 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
TOTALS	**2071**		**225**	**603**	**828**	

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. Differences are the bubble column reactor design which eliminates the agitator, and the immobilization of the catalyst onto solid particles rather than being dissolved in reaction medium. No commercial plants using this technology are currently operating. The total process input energy is about 4 times greater than the theoretical minimum energy. 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.
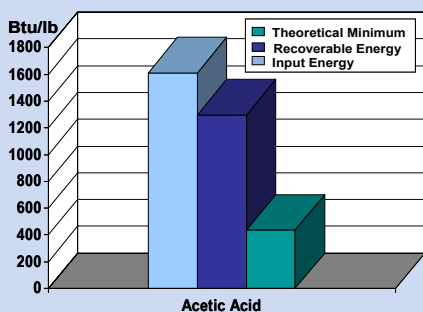
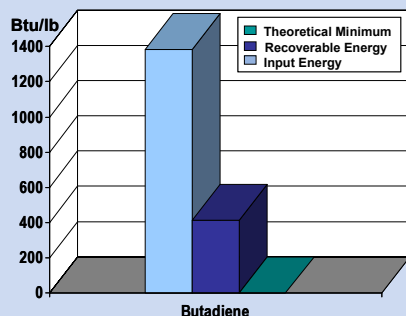| Acetic Acid via Methanol Carbonylation Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Carbonylation	118	8	19	715	734	57
Acetic Acid Refining	1326	92	144	419	563	43
TOTALS	**1444**		**163**	**1134**	**1297**	

Butadiene

This analysis looks at extractive distillation with DMF solvent (Nippon Zeon process) to recover butadiene from mixed C4 streams (butane, butene, butylene, butadiene). This is strictly a separation process with no chemical reaction, so no theoretical minimum is given. Distillation columns (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 Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss 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
TOTALS	**1103**		**44**	**369**	**413**	

Cumene

Solid Phosphoric Acid (SPA) Catalyzed – This exothermic process is based cumene via propylene alkylation of benzene with a solid phosphoric acid (SPA) catalyst (UOP design). 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 cumene recovery, 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
TOTALS	**1172**		**192**	**382**	**573**	

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 greater than the theoretical minimum. Cumene recovery is again the greatest source of energy and exergy losses, due to several distillation columns, most of which are operating 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.
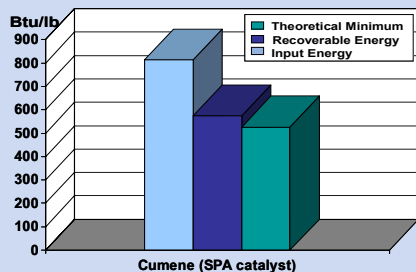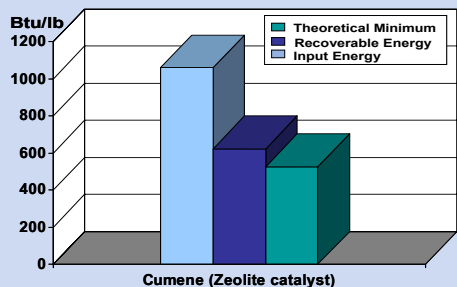

Cumene via Propylene Alkylation of Benzene (Zeolite-catalyzed) Process Sub-Section	Energy Loss Btu/lb	%	External Energy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Alkylation	231	17	64	187	250	40
Cumene Recovery	1154	83	240	133	373	60
TOTALS	**1385**		**304**	**319**	**623**	

AlCl₃ 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.
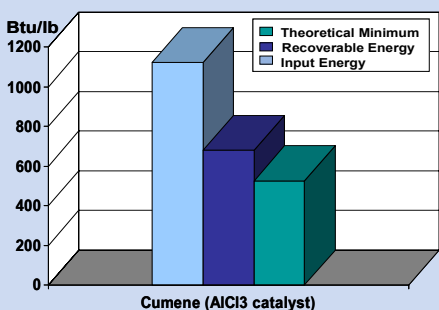
Cumene via Propylene Alkylation of Benzene (AlCl₃-catalyzed) Process Sub-Section	Energy Loss Btu/lb	%	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Total Exergy Loss Btu/lb	%
Alkylation	424	28	68	203	271	40
Catalyst Recovery	3	0	0	1	2	0
Cumene Recovery	1104	72	268	139	407	60
TOTALS	**1531**		**337**	**343**	**680**	

Energy/Exergy Losses by Unit Operation

Energy and exergy losses were compiled for unit operations and classes of equipment common to the 25 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. 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 most used separation technology and contributes to 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

Table 6. Energy and Exergy Losses in Unit Operations		
Unit Operation	Energy Loss (Tbtu/yr)	Exergy Loss (Tbtu/yr)
Endothermic Reaction	0	57
Exothermic Reaction	20	130
Distillation	408	172
Evaporation	0	4
Adsorption/Absorption	15	18
Crystallization	23	1
Cooling Water	867	119
Heat/Electrical/Steam Energy	1209	690

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.

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 to 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

There were no exergy losses in the endothermic reactions as the models are based on the effective energy input into each reactor. In practice, losses are inevitable due to energy transfer inefficiencies from the primary energy sources to the reactors.

Table 7. Energy Losses for Equipment (>500 Btu/lb)		
Type of Equipment	**No. of Items**	**Total Energy Loss Btu/lb**
Heat Exchangers	26	54,200
Columns	20	37,600
Compressors	2	1,190
Reactors	3	4,600
Miscellaneous	5	6,420

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 (not modeled separately in all cases). Overall, in all processes, heat exchanger accounts for the overwhelming majority of energy and exergy losses.

Table 8 provides details on the fifteen unit operations with the highest energy intensity (Btu/lb) 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. Over 20% the potential for economic energy recovery becomes much greater.

A number of technologies dominate the top fifteen energy consumers shown in Table 8. These include acrylonitrile, methanol, and styrene. 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 36-42%). Methanol has a similar profile. Styrene requires substantial cooling prior to recovery, but the energy quality is low, indicating little potential for additional energy recovery.

The ethylene oxide condenser has the highest energy-intensity by far, primarily due to cooling and refrigeration requirements. This is 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, it 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.

Table 8. Highest Energy-Consuming Equipment, Ranked by Energy Loss				
Chemical Technology	**Equipment Name**	**Total Energy Loss (Btu/lb)**	**External Energy Loss (Btu/lb)**	**Energy Quality (%)**
Ethylene Oxide	Condenser	11621	1752	15
MTBE	MTBE Column	8641	1355	16
Methanol –ICI LP	Methanol Column	7775	1015	13
Acrylonitrile (propylene)	Heat & Refrigeration Recovery	6727	2435	36
Acrylonitrile (propane)	Heat & Refrigeration Recovery	5516	2339	42
Styrene - Lummus	Air Cooler	3284	395	12
Methanol – Lurgi	Heat Recovery	2958	922	31
Acrylonitrile (propane)	C-101 Overhead Cooler	2718	293	11
Ammonia	Syn Gas Separator	2608	614	24
Acrylonitrile (propane)	HCN Stripper	2600	84	3
Acrylonitrile (propylene)	C-101 Overhead Cooler	2443	295	12
Formaldehyde	Reactor	2268	487	21
Acrylonitrile (propylene)	HCN Stripper	2073	42	2
Styrene – Fina	EB Column	1943	192	10
Ethyl Benzene - Badger	Benzene Fractionator	1850	757	41

Recommendations for Research

Energy and exergy analysis of the 25 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 9, in order of descending recoverable energy potential.

	Table 9. Summary of Recommended Research Opportunities for Chemical Products	
Chemical Product	**Recoverable Energy (10^{12} Btu/Year)**	**Research Recommendations**
Ethylene	261	Large opportunities exist due to high volume production 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&D areas that could reduce energy intensity include: • Low temperature, more selective retrofit reaction systems to replace pyrolysis and eliminate need for quenching • Novel separation concepts (hybrid systems) coupled with new ways of producing ethylene • Dehydrogenation or oxydehydrogenation based on ethane feedstock (dependent on price of NGLs versus petroleum) • New routes to ethylene based on alternative feedstocks (ethanol, methanol, methan/syngas, higher olefins), coupled with simpler recovery and purification technologies
Ammonia	115	Little incentive for R&D as market 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.
Ethylene Oxide	98	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: • Fluidized bed reactors • Liquid-phase oxidations, liquid-phase processes using hydroperoxide or hydrogen peroxide • Bioxidation of ethylene • Processes for richer EO-containing streams to reduce large recycle • Novel separations for richer EO streams, including carbonate system
Propylene	67	Currently nearly all propylene is produced as a coproduct with ethylene in naptha 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.
Terephthalic Acid (purified) (PTA)	55	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: • Novel separation schemes for solvent recovery and dehydration and for refining/purifying PTA • Process requiring less corrosive solvent • Entirely new concepts for producing PTA

Chemical Product	Recoverable Energy (10^12 Btu/Year)	Research Recommendations
		Table 9. Summary of Recommended Research Opportunities for Chemical Products
MTBE	53	Demand for MTBE is declining due to legislation banning its use as a gasoline additive. No research is warranted.
Methanol	36	Expectations for building methanol plants in the U.S. are not high, unless used as a means for bringing methane to market. Innovations could include: • Liquid phase processes for methanol production • Better process technologies for production of synthesis gas • Improved catalysts, including biocatalysts • Alternative feedstocks (methane, biomass) • Novel separation technologies to reduce distillation
Acrylonitrile	32	Conversion to acrylonitrile (ACN) takes place at high temperatures and requires a rapid quench of reaction gases to lower temperatures with a complex separation scheme (often with refrigeration). Novel ideas are needed to reduce energy intensity: • Fluidized beds • Recycle process with substitution of oxygen for air • Biocatalytic production of ACN • Novel concepts for difficult acetonitrile/acrylonitrile separations
Formaldehyde	31	It is uncertain what the process of choice will be for formaldehyde production (mixed-oxide versus silver catalyst). Possible improvements: • More selective, longer-life catalysts • New ways to recover formaldehyde (without polymerization)
Nitric Acid	24	Growth in nitric acid markets is stagnant, with little incentive for R&D. Current processes practice significant heat recovery. Lower temperature catalysts for ammonia oxidation could be an area for research if incentives were present.
Styrene	16	Current high temperature endothermic reaction requires preheating of feed and cooling of effluents with high energy burdens. R&D to reduce energy use: • Liquid phase lower temperature process with continuous removal of hydrogen • Novel separation technologies to remove hydrogen • Process using diluents other than steam • Alternative feedstock process
Ethylbenzene	16	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-Xylene	15	Considerable energy recovery is already practiced. New opportunities include: • New separation technologies, e.g., removing p-xylene during isomerization • Couple p-xylene process with downstream terephthalic acid process to achieve reductions in energy use (e.g., unique catalyst for oxidation)
Carbon Dioxide	15	Solvents for recovering carbon dioxide are limited and expensive, and could poison recycle gases. Possible areas for research: • Better solvents, especially adducts • Novel separations or hybrid separations with membranes, PSA, etc

Table 9. Summary of Recommended Research Opportunities for Chemical Products		
Chemical Product	**Recoverable Energy (10^12 Btu/Year)**	**Research Recommendations**
Vinyl Chloride	14	Large energy use and losses are due to the need to vaporize ethylene dichloride (EDC), crack at high temperature and then quench the reaction gas (done to minimize coking). In addition, many distillation systems are needed to separate HCl coproduct and purify vinyl chloride and EDC. Concepts to reduce reaction temperature and energy for separations include: • Cracking additives • Low-temperature catalysts • Alternative feedstocks, e.g., catalytic dehydrogenation of ethyl chloride • Novel separation systems to reduce distillation
Acetic Acid	6	Catalyst research continues to improve acetic acid production. Other research needs: • Novel separations to improve carbonylation routes (e.g., separation of gases from carbonylation reaction, supplementation of distillation) • Other routes to acetic acid (oxidation of butane, ethylene-based, oxidative dehydrogenation of ethane) • Acetic acid from biomass via chemical or biocatalysis
Cumene	5	All cumene goes to production of phenol and acetone. Demand for phenol is not balanced with demand for acetone (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 bisphenolA processes.
Butadiene	2	Almost all butadiene is present in C4 (butane and derivatives) streams from refineries and steam crackers, and little dedicated production exists. Improvements could be made in methods of separating butadiene from butane/butane/butadiene mixtures (new solvents, hybrid systems, membranes, PSA).

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Appendix A—Data Tables

Table A.1 Input, Actual Process, Minimum Theoretical, and Recoverable Energies

Table A-2. Energy and Exergy Losses at the Unit Operation Level, Btu/lb

Table A.1 Input, Actual Process, Minimum Theoretical and Recoverable Energies

	Process	Total Process Energy Input (Q_{IN}) Btu/lb	Total Process Exergy Input Btu/lb	Actual Process Exergy (Q_W) Btu/lb	Theoretical Minimum Process Energy Btu/lb	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Potentially Recoverable, Available Energy (Q_{LOSS}) Btu/lb	Recoverable, Available Energy % (Process Energy Input)	External Exergy Losses as % (Total Exergy Input)	Process Irreversibility (Internal exergy) Losses as % (Total Exergy Input)
1	Styrene (Lummus)	4,703	1,697	305	340	478	914	1,392	30%	28%	54%
2	Styrene (Fina/Badger)	3,365	1,122	369	340	410	1,081	1,491	44%	28%	73%
3	Vinyl Chloride	2,671	975	147	142	225	603	828	31%	23%	62%
4	Ethylbenzene (Mobil/Badger)	1,787	965	(236)	273	870	412	1,282	72%	72%	34%
5	Ethylbenzene (Lummus)	1,528	1,147	(231)	273	601	762	1,363	89%	52%	66%
6	Ethylene Oxide	7,741	5,735	(6,720)	734	2,096	10,360	12,456	161%	17%	83%
7	Ethylene (Braun)	8,656	5,534	326	650	1,806	3,402	5,208	60%	33%	61%
8	Ethylene (Kellogg)	8,139	5,035	217	650	1,167	3,651	4,818	59%	23%	73%
9	Carbon Dioxide	2,083	508	(426)	N/A	289	646	935	45%*	31%	69%
10	Acetic Acid	1,612	786	(512)	436	163	1,134	1,297	80%	13%	87%
11	Methanol (ICI LP)	4,883	871	(4,546)	802	1,289	4,128	5,417	111%	24%	76%
12	Methanol (Lurgi)	2,273	841	(4,132)	802	2,165	2,808	4,974	219%	44%	56%
13	ACN From Propylene	4,364	1,020	(8,015)	4,355	3,191	5,844	9,035	207%	35%	65%
14	ACN From Propane	5,381	1,392	(13,152)	5,509	3,129	11,415	14,544	270%	22%	78%
15	Formaldehyde	698	115	(3,209)	802	491	2,833	3,324	476%*	15%	85%

() Exothermic Reaction, net chemical conversion exergy inflow

N/A A separation process without chemical reaction

Table A.1 Input, Actual Process, Minimum Theoretical, and Recoverable Energies (continued)

	Process	Total Process Energy Input (Q_{IN}) Btu/lb	Total Process Exergy Input Btu/lb	Actual Process Exergy (Q_W) Btu/lb	Theoretical Minimum Process Energy Btu/lb	External Exergy Loss Btu/lb	Internal Exergy Loss Btu/lb	Potentially Recoverable, Available Energy (Q_{LOSS}) Btu/lb	Recoverable, Available Energy % (Process Energy Input)	External Exergy Losses as % (Total Exergy Input)	Process Irreversibility (Internal exergy) Losses as % (Total Exergy Input)
16	**Terephthalic Acid**	1,919	1,157	4,730	3,047	1,440	4,447	5,887	307%	124%	384%
17	**Butadiene**	1,382	468	55	N/A	44	369	413	30%	9%	79%
18	**Propylene**	4,548	3,047	1,440	846	227	1,892	2,119	47%	7%	62%
19	**p-Xylene (Isomerization)**	3,228	1,702	(133)	5	586	1,249	1,835	57%	32%	68%
20	**Nitric Acid**	232	207	(1,401)	1,953	492	1,117	1,609	694%	31%	69%
21	**Ammonia**	4,596	3,543	(351)	414	1,170	2,797	3,967	86%	30%	72%
22	**MTBE**	8,868	2,572	(135)	124	1,408	1,299	2,706	31%	52%	48%
23	**Cumene (SPA Cat)**	812	328	(245)	526	192	382	574	71%	34%	67%
24	**Cumene (Zeolite Cat)**	1,061	375	(248)	526	304	319	623	59%	49%	51%
25	**Cumene (AlCl₃ Cat.)**	1,124	440	(240)	526	343	337	680	61%	51%	50%

() Exothermic Reaction, net chemical conversion exergy inflow
N/A A separation process without chemical reaction

Table A-2. Energy and Exergy Losses at the Unit Operation Level, Btu/lb

#	Process		Reactions (Btu/lb)		Separations (Btu/lb)										Utilities (Btu/lb)	
			Endothermic	Exothermic	Distillation	Evaporation	Drying	Adsorption/Absorption	Extraction	Filtration	Membrane	Ion-exchange	Crystallization	Cooling Water	Heat/Electrical/Steam/etc Energy
1	Styrene (Lummus)	Energy	0		295									569	4,703
		Exergy	69		129									50	1,697
2	Styrene (Fina/Badger)	Energy	0		2,120									5,193	3,365
		Exergy	248		380									397	1,121
3	Vinyl Chloride	Energy	0		1,180					0				1,200	2,671
		Exergy	360		239					0				162	975
4	Ethyl Benzene (Mobil/Badger)	Energy	0	0	2,126									2,262	1,787
		Exergy	3	23	877									870	965
5	Ethylbenzene (Lummus)	Energy		0	1,841									166	1,528
		Exergy		536	687									40	1,131
6	Ethylene Oxide	Energy		0	441			0						14,630	7,741
		Exergy		4,047	516			903						2,579	5,735
7	Ethylene (Braun)	Energy	0	34	642			0						2,522	8,656
		Exergy	106	41	1,112			0						345	5,534
8	Ethylene (Kellogg)	Energy	0	0	1,071									4,830	8,139
		Exergy	492	100	1,087									382	5,035
9	Carbon Dioxide	Energy			1,001			377						2,299	2,083
		Exergy			253			486						286	508
10	Acetic A	Energy		0	1,394									1,332	1,612
		Exergy		714	507									138	786
11	Methanol (ICI-LP)	Energy	0	0	8,017			0						9,601	4,883
		Exergy	54	2,108	3,768			23						1,245	871
12	Methanol (Lurgi)	Energy	0	511	1,897			0						1,984	2,273
		Exergy	5	1,762	716			1						262	849

Table A-2. Energy and Exergy Losses at the Unit Operation Level, Btu/lb (continued)

	Process		Reactions (Btu/lb)		Separations (Btu/lb)										Utilities (Btu/lb)	
			Endothermic	Exothermic	Distillation	Evaporation	Drying	Adsorption/ Absorption	Extraction	Filtration	Membrane	Ion-exchange	Crystallization	Cooling Water	Heat/Electrical /Steam/etc Energy
13	Acrylonitrile (Propylene, SOHIO)	Energy		0	2,923	0		92						5,488	4,364
		Exergy		3,595	492	1,292		80						814	1,020
14	Acrylonitrile (Propane, SOHIO)	Energy		0	3,558	0		31						7,583	5,381
		Exergy		8,703	594	1,269		151						1,097	1,392
15	Formaldehyde	Energy		0										2,268	698
		Exergy		235										487	115
16	Terephthalic Acid	Energy		16	1,465								247	1,985	1,919
		Exergy		332	336								115	487	1,157
17	Butadiene	Energy			799									712	1,382
		Exergy			324									30	468
18	Propylene	Energy	0	72	1,117									3,376	4,548
		Exergy	851	159	325									310	3,560
19	p-Xylene	Energy		137	261									462	3,228
		Exergy		246	167									25	1,702

Table A-1. Energy and Exergy Losses at the Unit Operation Level, Btu/lb (continued)

#	Process		Reactions		Separations									Utilities	
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20	Nitric Acid	Energy		66				574						490	232
		Exergy		568				214						47	207
21	Ammonia	Energy	0	117										1,723	4,596
		Exergy	187	908										133	3,543
22	MTBE	Energy		261	8705									8,835	8,868
		Exergy		118	2522									1,384	2,572
23	Cumene (SPA Cat)	Energy		0	1,032									834	812
		Exergy		146	370									63	328
24	Cumene (Zeolite Cat)	Energy		174	1,019									797	1,061
		Exergy		230	331									120	375
25	Cumene (AlCl$_3$ Cat)	Energy		305	922									1,043	1,124
		Exergy		249	365									190	440
	TOTALS	**Energy**	**0**	**1,694**	**43,826**	**0**	**0**	**1,074**	**0**	**19**	**0**	**0**	**247**	**82,182**	**87,654**
		Exergy	**2,376**	**24,819**	**16,096**	**2,561**	**0**	**1,858**	**0**	**12**	**0**	**0**	**115**	**11,941**	**42,039**