The Top 50 Commodity Chemicals: Impact of Catalytic Process Limitations on Energy, Environment, and Economics

August 1995

Prepared for the U.S. Department of Energy,
Office of Industrial Technology (OIT)
Biological and Chemical Technologies
Research (BCTR) Program
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PNL-10684

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PNL-10684
UC-601

**The Top 50 Commodity Chemicals:
Impact of Catalytic Process Limitations
on Energy, Environment, and Economics**

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Executive Summary

The production processes for the top 50 U. S. commodity chemicals waste energy, generate unwanted byproducts, and require more than a stoichiometric amount of feedstocks. Pacific Northwest Laboratory^a has quantified this impact on energy, environment, and economics for the catalytically produced commodity chemicals. An excess of 0.83 quads of energy per year in combined process and feedstock energy is required. The major component, approximately 54%, results from low per-pass yields and the subsequent separation and recycle of unreacted feedstocks. Furthermore, the production processes, either directly or through downstream waste treatment steps, release more than 20 billion pounds of carbon dioxide per year to the environment. The cost of the wasted feedstock exceeds 2 billion dollars per year. Process limitations resulting from unselective catalysis and unfavorable reaction thermodynamic constraints are the major contributors to this waste. Advanced process concepts that address these problems in an integrated manner are needed to improve process efficiency, which would reduce energy and raw material consumption, and the generation of unwanted byproducts.

Many commodity chemicals are used to produce large volume polymer products. Of the energy and feedstock wasted during the production of the commodity chemicals, nearly one-third and one-half, respectively, represents chemicals used as polymer precursors. Approximately 38% of the carbon dioxide emissions are generated producing polymer feedstocks.

^a Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

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1.0 Introduction

Catalytically produced commodity chemicals represent an important cross-section of the U. S. chemical and petrochemical industry. The impact of the inefficiencies found in these production routes is magnified by the large annual volume of materials produced. The corresponding impact of these process inefficiencies on energy consumption, unwanted byproduct formation, and added economic burdens is a driver for process improvements. Identification of the most impactful areas for targeted research is a goal of the U. S. Department of Energy, Office of Industrial Technology.

The purpose of this study conducted for DOE by Pacific Northwest Laboratory (PNL) was to quantify the combined impact of energy, environment, and economics on the catalytically produced top 50 commodity chemicals. An initial estimate of the energy savings that would result from raising the overall process yields to their theoretical maximum concluded that an excess of 0.47 Q/yr was required (Tonkovich 1994). The 1994 study evaluated each product as if it were produced by a "black-box" single-pass process that had a linear relationship between process yield and energy. The current study examines each chemical production route in greater detail to describe realistic processes that are often multiple pass and incorporate energetically and environmentally expensive separation and reactant recycle steps. For example, a process that may have an overall yield of 90% was assumed to have a maximum process and feedstock energy savings of 10%. In reality, this process may have a per-pass yield of 10%, which corresponds to a 10% savings in feedstock energy, but up to a 90% savings in process energy. These revised numbers have been used in the calculations for this study.

Process limitations that account for possible energy savings were estimated and grouped. The primary process limitations are as follows: equilibrium limitations for the main reaction, equilibrium limitations for competing reactions, kinetic limitations for the main reaction, kinetic limitations from competing reactions (including overoxidation and over alkylation), catalyst deactivation, heat addition, heat removal, and mass transfer limitations. No attempt was made to assign fractional impact values for those chemicals subject to more than one problem. These limitations are interdependent and would necessitate further in-depth study to assess their true relative importance. The impact from each category was summed and normalized to prioritize the relative importance of the various process limitations.

The environmental impact associated with the production of the top 50 chemicals was partially estimated and quantified. The byproducts of the carbonaceous feedstocks were

cited. Carbon dioxide was the most common byproduct. It is either formed directly in the process or generated downstream by flaring carbonaceous byproducts or from other waste treatment conversion processes. In these cases, an equivalent carbon dioxide production value is calculated. For example, the primary side product for the production of ethylene oxide is carbon dioxide. The wasted feedstock is assumed to be fully converted to carbon dioxide in the amount of approximately 3.5 billion lb/yr. Another example is the production of styrene. While carbon dioxide is not produced directly, tars and other highly polymerized side products are co-produced with styrene. These heavy hydrocarbons are later incinerated and produce approximately 2.5 billion lb/yr of carbon dioxide.

Economic impact was estimated by summing the value of each wasted feedstock. This estimate is low and does not reflect potential capital and operating savings that would result from more efficient processes. The price per pound of each feedstock was obtained from Chemical Marketing Reporter (May 8, 1995).

2.0 Methodology

2.1 Energy Calculations

The maximum potential energy savings for each of the top 50 production routes is calculated in three steps. The first evaluates the partial impact on process energy by improving the overall process yield from current values to 100%:

$$E_{\text{saved-process}} = \frac{[\text{production rate}] \times [\text{process energy}] \times [1 - \text{fractional process yield}]}{[\text{fractional process yield}]}$$

The amount of feedstock to be processed is lowered, and thus the corresponding processing energy is reduced. The second step calculates the feedstock energy saved from improving the overall process efficiency and requiring fewer raw materials:

$$E_{\text{saved-feedstock}} = \frac{[\text{production rate}] \times [\text{feedstock energy-w/o double counting}]^b}{x [1 - \text{fractional process yield}] / [\text{fractional process yield}]}$$

The third step estimates the potential process energy savings that would result from raising per-pass yields. A new process energy (Btu/lb) is calculated which reflects a more efficient process that requires only a stoichiometric amount of feedstock:

$$\text{Process_energy}_{\text{new}} (\text{Btu/lb}) = [\text{Old process energy}] \times [\text{fractional process yield}]$$

This new process energy number is then used to calculate potential savings from driving the reaction to completion in a single pass.

$$E_{\text{saved-per_pass}} = \frac{[\text{Process_energy}_{\text{new}}] \times [\text{production rate}] \times [1 - \text{fractional per pass conversion}]}{[\text{fractional per pass conversion}]}$$

The total energy savings is calculated by summing the individual components.

$$E_{\text{total}} = E_{\text{saved-process}} + E_{\text{saved-per_pass}} + E_{\text{saved-feedstock}}$$

The amount of carbon dioxide formed is determined by first calculating the amount of feedstock that is converted to no-value byproducts. Many processes co-produce other

^b calculated by Tonkovich (1994)

saleable products, whose product selectivity is added with that of the desired (top 50) chemicals. Using combustion stoichiometry, the moles of carbon dioxide produced are calculated and converted into lb/year that are vented to the environment. Some processes do not produce carbon dioxide directly, but they do generate other no-value carbonaceous products, which are later flared or biologically converted to carbon dioxide. These are also included in the carbon dioxide calculation.

The extra feedstock cost is calculated by multiplying the excess lb/year feedstock required by the current value of this feedstock (as defined by Chemical Marketing Reporter).

The following are sample calculations used to determine byproduct yield, total feedstock conversion to product and byproducts, feedstock wasted, cost of feedstock wasted, and the carbon dioxide equivalent to the feedstock wasted.

2.2 Byproduct Yield Calculations

Byproduct data from the literature were expressed in one of four ways: 1) as a mole % yield based on a reactant, 2) as a difference between the total feedstock converted and the product yield, 3) as a weight fraction based on the amount of product produced, and 4) as a % selectivity to the byproduct based on the converted reactant. The first case requires no calculation.

The second case is used only in those circumstances of catalytic reforming of ethane to produce propylene, and naphtha to produce benzene, toluene, and xylene (BTX) and ethylbenzene, where all of the products are either separated and recovered or used as a mixture for olefin or gasoline manufacture:

$$\% \text{yield}_{\text{byproduct}} = 100 - \% \text{yield}_{\text{product}}$$

Example: production of hydrocarbon byproducts from catalytic reforming of ethane to propylene

$$\text{Propylene yield} = 1.71\%$$

$$\% \text{yield}_{\text{byproduct}} = 100 - 1.71 = 98.29\%$$

The third case requires a conversion of the weight % of the byproduct to a mole % based on the product multiplied by the product yield:

$$\% \text{yield}_{\text{byproduct}} = \text{yield}_{\text{product}} * (\text{wt fraction})_{\text{byproduct}} * (\text{mole wt})_{\text{product}} / (\text{mole wt})_{\text{byproduct}}$$

Example: byproduct yield of toluene from styrene synthesis:

$$\begin{aligned} \text{styrene yield} &= 90\% \\ \text{byproduct yield} &= 31 \text{ lb}_{\text{toluene}} / 1000 \text{ lb styrene} = .031 \\ \text{mole wt styrene} &= 104 \\ \text{mole wt toluene} &= 92 \end{aligned}$$

$$\% \text{yield}_{\text{toluene}} = 90\% * .031 * 104 / 92 = 3.15\%$$

The fourth case is applied to those circumstances where a byproduct or a co-product is formed and the selectivity is provided. This case requires a calculation of the yield by multiplying the reactant conversion by the selectivity of the process to the byproducts:

$$\% \text{yield}_{\text{byproduct}} = \% \text{conversion}_{\text{reactant}} * (\text{selectivity})_{\text{byproduct}}$$

Example: production of diethylene glycol and triethylene glycol during ethylene glycol manufacture:

$$\text{Total conversion of ethylene oxide} = 99\%$$

$$\text{Selectivity of ethylene oxide conversion to diethylene and triethylene glycol}$$

$$\text{products} = 0.1$$

$$\text{yield}_{\text{di- and tri-ethylene glycols}} = 99\% * 0.1 = 9.9\%$$

2.3 Total Wasted Feedstock Calculations

Total feedstock wasted is determined by calculating the amount of feedstock required to yield the amount of product and subtracting from that the amount that was converted to product and byproduct:

$$\text{feedstock}_{\text{wasted}} = \text{feedstock}_{\text{required}} * [1 - (\text{yield}_{\text{product}} + \text{yield}_{\text{byproduct}})]$$

$$\text{where the feedstock required} = \text{product made} / \text{yield}_{\text{product}}$$

Example: feedstock wasted for production of styrene:

styrene (mole wt = 104) produced = 8.94 billion lb/yr

styrene yield from ethylbenzene = 90 mol%

toluene byproduct yield = 3.15%

mole wt_{styrene} = 104

mole wt_{ethylbenzene} = 106

$$\begin{aligned} \text{ethylbenzene wasted} &= 8.94(10^8) / 104 / 90 * 106 * [100 - (90 + 3.15)] = 6.93(10^8) \text{ lb} \\ &= 0.693 \text{ billion lb} \end{aligned}$$

2.4 Cost of Wasted Feedstock Calculations

The annual cost of feedstock wasted is calculated by multiplying the amount of feedstock wasted by the unit cost of the feedstock:

$$\text{cost}_{\text{feedstock wasted}} = \text{unit feedstock cost} * \text{feedstock wasted}$$

Example: cost of ethylbenzene wasted during the production of styrene:

ethylbenzene wasted = 6.93(10⁸) lb

ethylbenzene unit cost = \$0.27/lb

cost of ethylbenzene = 6.93(10⁸) lb * \$0.27/lb = \$0.187(10⁹) = \$0.187 billion

2.5 Carbon Dioxide Calculations

The carbon dioxide equivalent to the feedstock wasted is determined by calculating the lb of CO₂ produced from each lb of feedstock and multiplying this amount by the lb of feedstock wasted:

$$\text{CO}_2 \text{ equivalent} = \frac{\text{lb}_{\text{feedstock wasted}}}{\text{lb}_{\text{CO}_2/\text{mol}_{\text{carbon}}}} \cdot \frac{\text{mol}_{\text{wt}_{\text{feedstock}}}}{\text{mol}_{\text{carbon}}/\text{mol}_{\text{feedstock}}} \cdot \text{mol}_{\text{carbon}}/\text{mol}_{\text{feedstock}} \cdot \text{mol}_{\text{carbon}}/\text{mol}_{\text{feedstock}}$$

Example: CO₂ equivalent of ethylbenzene wasted for production of styrene:

$$\text{ethylbenzene wasted} = 6.93(10^8) \text{ lb}$$

$$\text{mol wt}_{\text{ethylbenzene}} = 106$$

$$\text{mole carbon}_{\text{ethylbenzene}} = 8$$

$$\text{mole wt CO}_2 = 44$$

$$\text{CO}_2 \text{ equivalent} = [6.93(10^8)/106] \cdot 8 \cdot 44 = 2.3(10^8) \text{ lb}$$

3.0 Results and discussion

The production routes of the top 50 commodity chemicals were evaluated to assess the impact of process inefficiencies on energy, environment, and economics. An initial investigation (Tonkovich 1994) concluded that 0.47 Q/yr could be saved by improving the overall process yields to their theoretical maximum. The current study delves more deeply into the underlying phenomena that create these process inefficiencies and attempts to separate and quantify the possible energy savings from improving both the per-pass yields and the overall process yields. The environmental and economic impact of the waste that is co-generated with the saleable products are also quantified.

3.1 Energy Impact

The energy savings was divided into three main components: process energy saved from improving the overall yield, feedstock energy saved from raising the overall process yields, and the additional process energy saved from raising the per-pass yields. The primary assumption used to complete these calculations was a linear impact between yield improvement and energy savings. In reality, the relationship between energy and yield might vary from chemical to chemical and may stray from linearity.

In most cases, the overall process yield values were those cited earlier (Tonkovich 1994). In a few cases, new process yield data was obtained from the literature. These new values lower the calculated savings reported in the 1994 study from 0.47 to 0.38 Q/yr. The primary discrepancy is the omission of the BTX chemicals from the current study because they produce saleable byproducts rather than waste.

3.1.1 Process Energy Saved from Improving Overall Yields

For a generic process that sees a process yield improvement, there are fewer feedstocks required to achieve the desired production level. This reduction in the amount of material that must be heated, cooled, transported, and separated improves process efficiency. The calculated savings in process energy resulting from processes with higher overall yields summed over the 30 catalytically produced chemicals is 0.1459 Q/yr (see Table 1).

Table 1. Process Energy Savings from Overall Yield Improvements

Chemical	Process yield	Process selectivity	Process energy (Btu/lb)	Process energy savings (Q/yr)
Sulfuric acid	99.20	99.5	840	0.0006
Ammonia	87.12	99	8000	0.0425
Propylene	95.00	95	7500	0.0089
Nitric acid	94.05	95	1120	0.0011
Ethylene dichloride	94.05	99	1700	0.0017
Vinyl chloride	93.10	98	7500	0.0074
Benzene	N/A	N/A	1000	
Ethylbenzene	98.01	99	600	0.0001
MTBE	99.00	100	5600	0.0006
Styrene	90.00	90	5500	0.0055
Methanol	98.01	99	4250	0.0008
Formaldehyde	91.00	91	0	0.0000
Xylene	N/A	N/A	4400	
Toluene	N/A	N/A	4400	
p-Xylene	70.00	70	9600	0.0233
Terephthalic acid	85.50	90	5500	0.0053
Ethylene oxide	76.00	80	170	0.0003
Ethylene glycol	98.01	99	5600	0.0006
Cumene	97.02	99	1025	0.0001
Phenol	97.00	97	6500	0.0007
Acetic acid	99.00	99	4600	0.0002
Butadiene	67.50	90	22000	0.0337
Acrylonitrile	66.50	66.5	2600	0.0037
Propylene oxide	90.00	90	7000	0.0021
Vinyl acetate	90.00	90	6650	0.0020
Acetone	88.20	90	5630	0.0018
Cyclohexane	99.80	100	340	0.0000
Adipic acid	90.00	90	12500	0.0024
Caprolactam	90.25	95	3400	0.0005
Isobutylene	98.01	99		0.0000
Total				0.1459

3.1.2 Feedstock Energy Saved from Improving Overall Yields

When fewer feedstocks are needed to sustain a desired product production level, the required feedstock energy is reduced. The calculated savings in feedstock energy summed over all 30 catalytically produced chemicals equals 0.2380 Q/yr (see Table 2).

Table 2. Feedstock Energy Savings from Overall Yield Improvements

Chemical	Process yield	Feedstock (F) energy (Btu/lb)	F energy w/o double counting	F energy savings (Q/yr)
Sulfuric acid	99.20	0	0	0.0000
Ammonia	87.12	10500	10500	0.0558
Propylene	95.00	21000	21000	0.0250
Nitric acid	94.05	-	0	0.0000
Ethylene dichloride	94.05	7800	7800	0.0079
Vinyl chloride	93.10	-	0	0.0000
Benzene	N/A	18000	18000	
Ethylbenzene	98.01	18000	18000	0.0040
MTBE	99.00	21000	0	0.0000
Styrene	90.00	18500	1481.85	0.0015
Methanol	98.01	12200	12200	0.0022
Formaldehyde	91.00	19000	8771.1	0.0061
Xylene	N/A	18500	18500	
Toluene	N/A	18250	18250	
p-Xylene	70.00	18500	18500	0.0449
Terephthalic acid	85.50	18500	0	0.0000
Ethylene oxide	76.00	16000	16000	0.0281
Ethylene glycol	98.01	9100	0	0.0000
Cumene	97.02	20060	20060	0.0028
Phenol	97.00	18700	3.74	0.0000
Acetic acid	99.00	8300	0	0.0000
Butadiene	67.50	24750	24750	0.0379
Acrylonitrile	66.50	28000	13753.6	0.0196
Propylene oxide	90.00	21000	1050	0.0003
Vinyl acetate	90.00	12830	1154.7	0.0003
Acetone	88.20	15800	1393.56	0.0004
Cyclohexane	99.80	17100	17100	0.0001
Adipic acid	90.00	16000	2216	0.0004
Caprolactam	90.25	16000	2608	0.0004
Isobutylene	98.01	12000	12000	0.0003
Total				0.2380

3.1.3 Process Energy Saved from Improving Per-Pass Yields

Many processes involve multiple passes to achieve high overall process yields. A generic process may only achieve a fractional conversion in any single pass and must rely on downstream reactant separation and recycle to the reactor. The energy that is required from these multi-pass processes is much higher than those that produce saleable chemicals in a single pass. A new process energy (Btu/lb) is calculated to account for process yield improvements. Previously reported energy values (Lipinsky and Widrig, 1994) are multiplied by the maximum fractional improvement in process yield. Processes that do not require feedstocks above stoichiometric amounts will require less energy per pound to produce. These new process energy numbers are then used to calculate potential savings by assuming that non-unity per-pass conversions could be converted to a single-pass process (see Table 3). Improving the per-pass process efficiency would save 0.4482 Q/yr.

Table 3. Process Energy Savings from Per-Pass Yield Improvements

Chemical	Per-pass conversion	Old process energy (Btu/lb)	New process energy (Btu/lb)	Process energy savings
Sulfuric acid	99.70	840	833.24	0.0002
Ammonia	20.0	8000	6817.26	0.1961
Propylene	60.0	7500	7105.26	0.0642
Nitric acid	99.0	1120	1049.14	0.0002
Ethylene dichloride	95.0	1700	1592.45	0.0013
Vinyl chloride	60.0	7500	6944.15	0.0367
Benzene	90.0	1000	-	-
Ethylbenzene	99.0	600	587.82	0.0001
MTBE	99.0	5600	5543.43	0.0006
Styrene	70.0	5500	4888.89	0.0131
Methanol	7.0	4250	4163.71	0.0338
Formaldehyde	99.0	0	0.00	0.0000
Xylene	80.0	4400	-	-
Toluene	90.0	4400	-	-
p-Xylene	18.0	9600	5485.71	0.0255
Terephthalic acid	90.0	5500	4567.25	0.0026
Ethylene oxide	15.0	170	116.32	0.0005
Ethylene glycol	99.0	5600	5486.30	0.0003
Cumene	91.0	1025	993.52	0.0004
Phenol	50.0	6500	6298.97	0.0117
Acetic acid	90.0	4600	4553.54	0.0016
Butadiene	75.0	22000	11407.41	0.0091
Acrylonitrile	95.0	2600	1290.23	0.0002
Propylene oxide	22.0	7000	6222.22	0.0131
Vinyl acetate	15.0	6650	5911.11	0.0134
Acetone	50.0	5630	4876.78	0.0058
Cyclohexane	99.0	340	339.32	0.0000
Adipic acid	10.0	12500	11111.11	0.0175
Caprolactam	95.0	3400	3032.69	0.0002
Isobutylene	99.0		0.00	0.0000
Total				0.4482

A total energy savings of 0.8320 Q/yr could be realized by improving both the overall and per-pass process efficiencies (see Table 4). These numbers were calculated in the attached spreadsheet (top50proc_calc.xls).

Table 4. Total Energy Savings

Chemical	Process Energy savings-1 ^c	Feedstock Energy savings	Process Energy savings-2 ^d	Sum of Energy savings
Sulfuric acid	0.0006	0.0000	0.0002	0.0008
Ammonia	0.0425	0.0558	0.1961	0.2944
Propylene	0.0089	0.0250	0.0642	0.0981
Nitric acid	0.0011	0.0000	0.0002	0.0013
Ethylene dichloride	0.0017	0.0079	0.0013	0.0108
Vinyl chloride	0.0074	0.0000	0.0367	0.0441
Benzene	-	-	-	0.0000
Ethylbenzene	0.0001	0.0040	0.0001	0.0042
MTBE	0.0006	0.0000	0.0006	0.0012
Styrene	0.0055	0.0015	0.0131	0.0200
Methanol	0.0008	0.0022	0.0338	0.0367
Formaldehyde	0.0000	0.0061	0.0000	0.0061
Xylene	-	-	-	0.0000
Toluene	-	-	-	0.0000
p-Xylene	0.0233	0.0449	0.0255	0.0936
Terephthalic acid	0.0053	0.0000	0.0026	0.0078
Ethylene oxide	0.0003	0.0281	0.0005	0.0289
Ethylene glycol	0.0006	0.0000	0.0003	0.0009
Cumene	0.0001	0.0028	0.0004	0.0034
Phenol	0.0007	0.0000	0.0117	0.0124
Acetic acid	0.0002	0.0000	0.0016	0.0018
Butadiene	0.0337	0.0379	0.0091	0.0806
Acrylonitrile	0.0037	0.0196	0.0002	0.0235
Propylene oxide	0.0021	0.0003	0.0131	0.0155
Vinyl acetate	0.0020	0.0003	0.0134	0.0157
Acetone	0.0018	0.0004	0.0058	0.0081
Cyclohexane	0.0000	0.0001	0.0000	0.0001
Adipic acid	0.0024	0.0004	0.0175	0.0204
Caprolactam	0.0005	0.0004	0.0002	0.0011
Isobutylene	0.0000	0.0003	0.0000	0.0003
Total				0.8320

^c calculated from overall yield improvements.

^d calculated from per pass yield improvements.

3.2 Environmental Impact

The generation of carbonaceous products is often accompanied by the formation of carbon dioxide. In some processes it is produced directly; in others, unwanted carbonaceous byproducts are later incinerated or biologically converted. In either case, the cumulative effect exceeds 20.9 billion pounds of carbon dioxide released during the production of the top 50 chemicals (see Table 5). These numbers were calculated using the attached spreadsheet (top50proc_calc.xls).

Relative to the annual total carbon dioxide produced in the U. S. from fossil fuel sources, 2.75 trillion pounds (C & EN News, March 13, 1989), production of the top 50 chemicals accounts for approximately 0.76% of the total annual carbon dioxide emissions in the United States.

Table 5. Carbon Dioxide Production

Chemical	Feedstock-1	CO ₂ -1 (bil-lb/yr)	Feedstock-2	CO ₂ -2 (bil-lb/yr)	Total CO ₂
Sulfuric acid	SO ₂				
Ammonia	methane				
Propylene	propane				
Nitric acid	ammonia				
Ethylene dichloride	ethylene	0.821	chlorine		0.821
Vinyl chloride	ethylene dichloride	1.381			1.381
Benzene	naphtha				-
Ethylbenzene	ethylene	0.092	benzene	0.556	0.648
MTBE	methanol	0.096	isobutylene	0	0.096
Styrene	ethylbenzene	2.298			2.298
Methanol	carbon monoxide	0.213	hydrogen		0.213
Formaldehyde	methanol	1.080			1.080
Xylene	naphtha				-
Toluene	naphtha				-
p-Xylene	xylene				-
Terephthalic acid	p-xylene	0.629			0.629
Ethylene oxide	ethylene	3.512			3.512
Ethylene glycol	ethylene oxide	0.082			0.082
Cumene	benzene	0.000	propylene	0.000	
Phenol	cumene	0.483			0.483
Acetic acid	methanol	0.027	carbon monoxide	0.323	0.350
Butadiene	butene	4.990			4.990
Acrylonitrile	propylene	1.629	ammonia		1.629
Propylene oxide	propylene	0.683	iso-butane	0.910	1.593
Vinyl acetate	ethylene	0.302	acetic acid	0.000	0.302
Acetone	cumene				
Cyclohexane	benzene	0.014	hydrogen		0.014
Adipic acid	cyclohexane	0.352	nitric acid		0.352
Caprolactam	cyclohexane	0.348			0.348
Isobutylene	n-butane	0.082			0.082
Total					20.903

3.3 Economic Impact

The extra feedstock required to compensate for process inefficiencies results in economic losses. The wasted moles of feedstock were calculated and assigned dollar values from Chemical Marketing Reporter. Summed over all of the top catalytically produced chemicals, over two billion dollars is used to purchase feedstocks that are

eventually converted to carbon dioxide. These numbers were calculated in the attached spreadsheet (top50proc_ref.xls).

Table 6. Economic Impact

Chemical	Feedstock-1 (F-1)	F-1 (bil lb/yr)	F-1 cost (\$/lb)	F-1 wasted (bil \$)	Feedstock-2 (F-2)	F-2 (bil lb/yr)	F-2 cost (\$/lb)	F-2 wasted (bil \$)
Sulfuric acid	SO ₂	0.467	0.115	0.054				
Ammonia	methane	0.625						
Propylene	propane	0						
Nitric acid	ammonia	0.275	0.130	0.036				
Ethylene dichloride	ethylene	0.261	0.280	0.073	chlorine			
Vinyl chloride	ethylene dichloride	1.553	0.170	0.264				
Benzene	naphtha		0.148					
Ethylbenzene	ethylene	0.029	0.280	0.008	benzene	0.164	0.143	0.023
MTBE	methanol	0.096	0.068	0.007	i-butylene	0	0.310	
Styrene	ethylbenzene	0.692	0.270	0.187				
Methanol	carbon monoxide	0.155			hydrogen			
Formaldehyde	methanol	0.736	0.068	0.050				
Xylene	naphtha		0.148					
Toluene	naphtha		0.148					
p-Xylene	xylene	0.841	0.159	0.134				
Terephthalic acid	p-xylene	0.190	0.360	0.068				
Ethylene oxide	ethylene	1.117	0.280	0.313				
Ethylene glycol	ethylene oxide	0.041	0.450	0.018				
Cumene	benzene	0	0.143		propylene	0	0.223	
Phenol	cumene	0.146	0.200	0.029				
Acetic acid	methanol	0.027	0.068	0.002	carbon monoxide	0.206		
Butadiene	butene	1.588	0.260	0.413				
Acrylonitrile	propylene	0.654	0.223	0.146	ammonia			
Propylene oxide	propylene	0.217	0.223	0.048	iso-butane	0.300		
Vinyl acetate	ethylene	0.096	0.280	0.027	acetic acid	0	0.330	
Acetone	cumene		0.200					
Cyclohexane	benzene	0.004	0.143	0.001	hydrogen			
Adipic acid	cyclohexane	0.112	0.181	0.020	nitric acid			
Caprolactam	cyclohexanone	0.129	0.730	0.094				
Isobutylene	n-butane	0.027	0.260	0.007				
Total								2.022

3.4 Process Limitations

The production routes of the catalytically produced top 50 chemicals have eight key process limitations, categorized as follows:

- Lim 1 = Equilibrium-limited (main reaction)
- Lim 2 = Equilibrium-limited (competitive reactions)
- Lim 3 = Kinetics-limited (main reaction)
- Lim 4 = Kinetics-limited (competing reactions)
- Lim 5 = Catalyst deactivation
- Lim 6 = Heat addition limited
- Lim 7 = Heat removal limited
- Lim 8 = Mass transfer limited

The potential energy savings from each chemical have been cross-referenced against the process limitation(s) (see Table 7).

Those processes affected by more than one limitation were not assigned fractional impact values. The total possible energy savings was inserted in each category. The sums of each category were normalized to determine a relative importance of the various process limitations. Three categories account for approximately three-quarters of all limitations: equilibrium limitations for the main reaction, kinetic limitations for the main reaction, and kinetic limitations resulting from competing reactions.

Table 7. Process Limitations

Chemical	Lim-1	Lim-2	Lim-3	Lim-4	Lim-5	Lim-6	Lim-7	Lim-8
Sulfuric acid		0.0008						
Ammonia	0.2944		0.2944					
Propylene				0.0981				
Nitric acid	0.0013							
Ethylene dichloride				0.0108				
Vinyl chloride				0.0441			0.0441	
Benzene								
Ethylbenzene		0.0042		0.0042				
MTBE	0.0012						0.0012	0.0012
Styrene						0.0200		0.0200
Methanol	0.0367		0.0367					
Formaldehyde	0.0061			0.0061				
Xylene								
Toluene								
p-Xylene		0.0936						
Terephthalic acid			0.0078	0.0078				
Ethylene oxide				0.0289	0.0289		0.0289	
Ethylene glycol								
Cumene				0.0034				
Phenol				0.0124				
Acetic acid		0.0018		0.0018				
Butadiene				0.0806	0.0806		0.0806	
Acrylonitrile				0.0235				
Propylene oxide				0.0155				
Vinyl acetate				0.0157			0.0157	0.0157
Acetone				0.0081				
Cyclohexane							0.0001	
Adipic acid				0.0204			0.0204	
Caprolactam				0.0011				
Isobutylene				0.0003	0.0003	0.0003		
Normalized %	22.34	6.61	22.30	25.19	7.23	1.34	12.57	2.43

3.5 Impact on Top 12 Polymers

Many of the commodity chemicals are precursors for polymer products. A study to describe the top 12 polymer production processes and the associated energy consumption is under preparation (Lipinsky and Wesson, 1995). Table 8 presents the percentage of each commodity chemical used as a polymer feedstock, the total excess process and feedstock energy, the value of wasted feedstock, and the amount of carbon dioxide that is generated producing commodity chemicals that later become the top 12 polymers. This information is included in the attached spreadsheet (top50proc_calc.xls).

An excess of 0.2734 Q/yr is needed to produce the polymer precursor chemicals. This represents nearly one-third of the total extra energy required for the top 50 commodity chemicals. Approximately 1 billion dollars are wasted to purchase excess feedstocks. This equates to nearly one-half of the total dollar value wasted to produce all of the commodity chemicals. Over 7.8 billion pounds of carbon dioxide are co-produced with the polymer precursor chemicals; this represents approximately 38% of the total.

Table 8. Impact of Commodity Chemicals on Top 12 Polymers

Chemical	% used to produce top 12 polymers	Total energy savings (Q/yr)	Wasted feedstock (bil \$)	CO2 generated (bil lb/yr)
Sulfuric acid				
Ammonia				
Propylene	46	0.0451	0.0000	
Nitric acid	10	0.0001	0.0036	
Ethylene dichloride	88	0.0095	0.0643	0.7225
Vinyl chloride	84	0.0370	0.2218	1.1600
Benzene	64			
Ethylbenzene				
MTBE				
Styrene	77	0.0154	0.1439	1.7695
Methanol	27	0.0099	0.0000	0.0575
Formaldehyde	29	0.0018	0.0146	0.3132
Xylene				
Toluene	4			
p-Xylene	100	0.0936	0.1337	
Terephthalic acid	99	0.0078	0.0677	0.6227
Ethylene oxide	28	0.0081	0.0876	0.9834
Ethylene glycol	29	0.0003	0.0054	0.0238
Cumene	63	0.0021	0.0000	
Phenol	54	0.0067	0.0158	0.2608
Acetic acid				
Butadiene	16	0.0129	0.0660	0.7984
Acrylonitrile	18	0.0042	0.0262	0.2932
Propylene oxide	17	0.0026	0.0082	0.2708
Vinyl acetate				
Acetone				
Cyclohexane	82	0.0000	0.0005	0.0115
Adipic acid	74	0.0151	0.0150	0.2605
Caprolactam	87	0.0010	0.0819	0.3028
Isobutylene				
Total		0.2734	0.9560	7.8505
% of top 50 total		32.86	47.29	37.56

4.0 Advanced Process Concepts

The process improvements needed to achieve the energy savings assumed in this study represent, in many cases, dramatic changes to existing processes. Realization of these improvements will not occur through incremental improvements in catalysts or process design. The complex underlying problems are not intractable, but they do require new approaches that address the interdependent problems and process limitations.

A strategy to integrate catalysis design and development with reactor design is proposed to achieve these goals. Most of the process inefficiencies result from kinetic, thermodynamic, and transport limitations. In general, catalysis can address kinetic limitations, while reactor design addresses thermodynamic and transport limitations. For complex problems, both approaches must be integrated.

4.1 Catalysis Design and Development

Catalysis plays a direct role in the production of 30 of the top 50 commodity chemicals, and an indirect one for six other chemicals. Catalyst improvements have a direct impact in lowering production temperatures, increasing per-pass yields, and decreasing unwanted byproducts.

Catalysis alone, however, will not maximize process efficiency. All reactions progress along the lowest energy pathway toward thermodynamic equilibrium, although many reactions are operated far from equilibrium and are controlled by competing reaction rates. The addition of a catalyst increases reaction rates but cannot change the thermodynamic driving force that provides the direction for the reaction. If for a given set of conditions, an equilibrium yield of only 30% were possible, then the addition of a catalyst would allow the reactor to achieve a 30% yield in less time.

For many chemicals, it is thermodynamics that limits process efficiency. The production of ammonia is one example where the conversion is dictated by thermodynamics. At the current processing temperatures and pressures, conversions range between 10% and 30% per pass. Higher per-pass yields are possible by changing pressure, temperature, or composition but not by improving the catalyst.

4.2 Reactor Design

The selection of an appropriate reactor design is equally important in developing a catalytic reactor. Issues of heat and mass transport are addressed through reactor design and are vital to the efficiency and safety of the production processes. Many of the commodity chemical production routes are highly exothermic. The problems arising from inefficient heat removal and mass transport range from undesirable product distributions to thermal runaway and potential explosions.

Reactor design, in conjunction with appropriate catalyst selection, can overcome adverse thermodynamic constraints. Equilibrium is defined for a static system based on temperature, pressure, and composition. For a flowing system, the local values of these parameters set reaction driving forces. Novel reactor designs that alter *in situ* temperature, pressure, or composition change local driving forces. The result is a reactor that appears to "beat" equilibrium. This concept has been put into practice for the production of MTBE (~24 billion lb/yr).

MTBE is produced through reactive distillation, and yields approach 99% per pass. The product is simultaneously removed via distillation as the reaction proceeds, pushing the reaction further toward completion. Yields of this magnitude are only possible with an appropriate reactor design that couples separation and reaction.

For the case of ammonia, a reactor design that separates ammonia as it is produced could achieve higher per-pass yields than those observed commercially. Local reductions in the ammonia partial pressure add a forward driving force that would push this reaction toward completion.

Redesigned reactors include, but are not limited to, the generic class of separative reactors. This emerging field represents a suite of enabling technologies that have the potential to improve the production yields for many reactions. These include ammonia, styrene, ethylene oxide, propylene oxide, methanol, butadiene, hydrogen, and many others.

True process efficiency gains for the commodity chemicals will best be achieved through the integration of catalysis and an appropriate reactor design. Each alone will not maximize process efficiency gains, but developed in concert the limitations from both kinetics and thermodynamics can be overcome.

4.3 Integrated Process Design

This section describes the problems associated with the top 50 production processes and possible advanced process concepts to mitigate those issues. The process limitations cited for the production routes of the 30 catalytically produced chemicals are divided into the following concepts:

- **Concept 1: Thermodynamic Limitations on Per-Pass Conversion**

Problem: The production of several chemicals, including ammonia, methanol, and styrene, has a limited conversion per pass dictated by thermodynamics. The operating temperature, pressure, and feed composition result in low yields per pass. This situation leads to an added reactant and product separation unit operation, followed closely by a reactant recycle loop. The energy required to heat, cool, separate, and recycle feedstocks makes these processes energy-intensive.

Potential solution: Product separation during reaction increases the thermodynamic driving force and allows the reaction to continue toward completion. The coupling of reaction and separation requires melding two unit operations into one to exploit process synergy. The requisite operating conditions (temperature, pressure, and chemical environment) must be matched to successfully join these operations. In addition, the separation medium must remain catalytically inert to the reactants. Several successful examples of this concept have been described in the literature, and one successful commercial operation (reactive-distillation) is in use for the production of MTBE.

The types of separative reactors include, but are not limited to, reactive-distillation, membrane reactors, pressure-swing adsorbers/reactors, and chromatographic reactors.

Concept 1

- **Concept 2: Kinetic Limitations - Low Catalyst Activity**

Problem: The production of several chemicals, including ammonia and methanol, has a low process efficiency because of kinetic constraints. The activity of the catalysts is fairly low, or the reaction conditions must be kept modest to prevent undesired side reactions.

Potential solution: More active catalysts would result in shorter contact times, smaller reactor volumes, and increased process efficiency.

Concept 2

- **Concept 3: Kinetic Limitations - Low Catalyst Selectivity**

Problem: The production of several chemicals, including ethylene oxide, butadiene, and acrylonitrile, has a low process efficiency because of kinetic constraints. The selectivity of the catalysts is low and undesired side reactions result in the generation of no-value byproducts.

Potential solution: More selective catalysts would result in a decrease in the generation of byproducts and increase process efficiency.

- **Concept 4: Coupled Kinetic and Thermodynamic Limitations**

Problem: The production of several chemicals, including ethylene oxide, propylene oxide, and formaldehyde, has a low process efficiency because of coupled kinetic and thermodynamic constraints. The desired products are more reactive than the feedstock and rapidly overoxidize to carbon dioxide. In addition, there is a strong thermodynamic driving force to produce carbon oxides, rather than the desired intermediate product.

Potential solution: More selective catalysts would decrease the generation of byproducts and increase process efficiency. However, catalyst development can not mitigate the thermodynamic driving force to overoxidize the product. This advanced concept controls the oxygen addition to favor the desired reactions by changing the local oxygen partial pressures that dictate thermodynamic driving forces.

Concept 4

- **Concept 5: Transport Limitations**

Problem: The production of several chemicals, including ethylene oxide and adipic acid, has a low process efficiency because of transport limitations. The highly exothermic reactions generate heat at a faster rate than it can be removed with conventional methods. To counter this problem, a diluent is often added to the feed to reduce the heat generated per unit volume. As a result the process must heat, transport, and cool excess material that in some cases represents a volume exceeding 10 times that of the feedstocks.

Potential solution: Improved heat removal technologies would reduce or eliminate the amount of diluent needed to ensure safe operation of the reactor. Higher production rates per unit volume would increase the process efficiency.

- **Concept 6: Transport, Kinetic, and Thermodynamic Limitations**

Problem: The production of several chemicals, including ethylene oxide and adipic acid, has a low process efficiency because of coupled transport, kinetic, and thermodynamic limitations. The conversions per pass are maintained at a low level to safely operate the reactor with a high product selectivity.

Potential solution: New technologies that simultaneously mitigate all three limitations are required to improve the process efficiency. Improved heat transfer coupled with new catalysts and reactor designs to mitigate the process limitations is required.

5.0 Conclusions

The production routes associated with the catalytically produced commodity chemicals consume additional energy and raw materials beyond those necessary to produce the desired level of saleable products. In this study waste is quantified in terms of energy, environment, and economics. It was found that 0.83 quads of energy are wasted, 20.9 billion pounds of carbon dioxide are released to the atmosphere, and over 2 billion dollars are spent to purchase feedstocks that are converted to waste.

The process inefficiencies that give rise to this waste are a function of both kinetics and thermodynamics. Traditional approaches to overcoming these limitations, namely catalyst development, are an important component to the solution. Alone, however, catalyst selection will not overcome many of the problems. Integration of catalyst development and reactor design is necessary to counter the process limitations and reduce the associated energy, environmental, and economic burdens.

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APPENDIX I

Potential Feedstock and Process Energy Savings Calculations

(attached file: top50proc_calc.xls)

Chemical	lb (bil) 92	Overall process yield	Conversion per Pass	Selectivity	Per pass yield	Maximum E savings from overall process improvements (P+F) – 1994 study	Maximum E savings from per pass yield improvements and overall process yield improvements
Sulfuric acid	88.8	99.2015	99.7	99.5	99.2015	0.0006	0.0008
Nitrogen	58.7						
Oxygen	42.38						
Ethylene	40.41						
Ammonia	35.95	87.12	20	99	19.8	0.0857	0.2944
Lime	34.72						
Phosphoric acid	25.36						
Sodium hydroxide	24.02						
Propylene	22.6	95	60	95	57	0.0322	0.0981
Chlorine	22.28						
Sodium carbonate	20.89						
Urea	16.84						
Nitric acid	16.08	94.05	99	95	94.05	0.0011	0.0013
Ethylene dichloride	15.94	94.05	95	99	94.05	0.0090	0.0108
Ammonium nitrate	15.33						
Vinyl chloride	13.23	93.1	60	98	58.8	0.0069	0.0441
Benzene	12.01	N/A	90	N/A	N/A	0.0639	0.0000
Ethylbenzene	10.99	98.01	99	99	98.01	0.0001	0.0042
MTBE	10.86	99	99	100	99	0.0006	0.0012
Carbon dioxide	10.79						
Styrene	8.94	90	70	90	63	0.0396	0.0200
Methanol	8.73	98.01	7	99	6.93	0.0029	0.0367
Formaldehyde	6.98	91	99	91	90.09	0.0005	0.0061
Xylene	6.38	N/A	80	N/A	N/A	0.0409	0.0000
Toluene	6.03	N/A	90	N/A	N/A	0.0393	0.0000
Hydrochloric acid	5.75						
p-Xylene	5.66	70	18	70	12.6	0.0470	0.0936
Terephthalic acid	5.64	85.5	90	90	81	0.0032	0.0078
Ethylene oxide	5.56	76	15	80	12	0.0216	0.0289
Ethylene glycol	5.12	98.01	99	99	98.01	0.0006	0.0009
Ammonium sulfate	4.72						
Cumene	4.57	97.02	91	99	90.09	0.0001	0.0034
Potash	3.76						
Phenol	3.71	97	50	97	48.5	0.0036	0.0124
Acetic acid	3.6	99	90	99	89.1	0.0021	0.0018
Butadiene	3.18	67.5	75	90	67.5	0.0510	0.0806
Carbon black	3.02						
Acrylonitrile	2.83	66.5	95	66.5	63.175	0.0122	0.0235
Propylene oxide	2.7	90	22	90	19.8	0.0022	0.0155
Vinyl acetate	2.66	90	15	90	13.5	0.0018	0.0157
Titanium dioxide	2.53						
Acetone	2.39	88.2	50	90	45	0.0020	0.0081
Cyclohexane	2.21	99.8	99	100	99	0.0000	0.0001
Aluminum sulfate	2.18						
Sodium silicate	1.8						
Adipic acid	1.75	90	10	90	9	0.0025	0.0204
Calcium chloride	1.39						
Caprolactam	1.38	90.25	95	95	90.25	0.0006	0.0011
Sodium sulfate	1.34						
Isobutylene	1.29	98.01	99	99	98.01	0.0003	0.0003
Sum	655.98					0.4740	0.8320
normalized fraction							
%							

Chemical	feedstock	Feedstock-1 wasted (bil lb/yr)	Feedstock-2 wasted (bil lb/yr)	Environ. waste = equiv. CO2 generated - feedstock-1	Environ. waste = equiv. CO2 generated - feedstock-2	\$/lb of feedstock #1	\$/lb of feedstock #2	notes (May 1, 1995 Chem Marketing Reporter)	\$/yr wasted feedstocks
Sulfuric acid	SO2	0.467		0		0.115		230/ton	0.053705
Nitrogen									
Oxygen									
Ethylene									
Ammonia	methane	0.625							0
Lime									
Phosphoric acid									
Sodium hydroxide									
Propylene	propane	0							0
Chlorine									
Sodium carbonate									
Urea									
Nitric acid	ammonia	0.275				0.13		260/ton	0.03575
Ethylene dichloride	ethylene, chlorine	0.261		0.821		0.28	0.1075		0.07308
Ammonium nitrate									
Vinyl chloride	ethylene dichloride	1.553		1.381		0.17			0.26401
Benzene	naptha							.88/gal	0
Ethylbenzene	ethylene, benzene	0.029	0.164	0.092	0.556	0.28	0.1428	1.05/gal benz	0.0315392
MTBE	methanol, isobutylene	0.096	0	0.096	0	0.0683	0.31	.45/gal meth	0.0065568
Carbon dioxide									
Styrene	ethylbenzene	0.692		2.298		0.27			0.18684
Methanol	CO, H2	0.155		0.213					0
Formaldehyde	methanol	0.736		1.08		0.0683		.45/gal meth	0.0502688
Xylene	naptha							.88/gal	0
Toluene	naptha							.88/gal	0
Hydrochloric acid									
p-Xylene	xylenes	0.841				0.159		1.15/gal	0.133719
Terephthalic acid	p-xylene	0.19		0.629		0.36			0.0684
Ethylene oxide	ethylene	1.117		3.512		0.28			0.31276
Ethylene glycol	oxide	0.041		0.082		0.45			0.01845
Ammonium sulfate									
Cumene	benzene, propylene	0	0	0		0.1428	0.2225	1.05/gal benz	0
Potash									
Phenol	cumene	0.146		0.483		0.2			0.0292
Acetic acid	CO	0.027	0.206	0.027	0.323	0.0683		.45/gal meth	0.0018441
Butadiene	butene	1.588		4.99		0.26			0.41288
Carbon black									
Acrylonitrile	propylene, ammonia	0.654		1.629		0.2225	0.13		0.145515
Propylene oxide	propylene,iso -butane	0.217	0.3	0.683	0.91	0.2225			0.0482825
Vinyl acetate	ethylene, acetic acid	0.096	0	0.302		0.28	0.33		0.02688
Titanium dioxide									
Acetone	cumene					0.2			0
Cyclohexane	benzene, hydrogen	0.004	0.004	0.014		0.1428		1.05/gal benz	0.0005712
Aluminum sulfate									
Sodium silicate									
Adipic acid	cyclohexane, nitric acid	0.112	0	0.352		0.1805	0.1825	1.17/gal cyclo	0.020216
Calcium chloride									
Caprolactam	cyclohexane	0.129		0.348		0.73			0.09417
Sodium sulfate									
Isobutylene	n-butane	0.027		0.082		0.26			0.00702
Sum				19.114	1.789				2.0216576
					20.903				
normalized fraction									
%									

Chemical	Equilibrium-limited (main rxn)	Equilibrium-limited (competitive rxns)	Kinetics-limited (main rxn)	Kinetics-limited (competing rxns)	Catalyst deactivation	Heat addition limited	Heat removal limited	Mass transfer limited	Cat. Sel.	Cat. Conv.
Sulfuric acid		0.0008							99.5	99.7
Nitrogen										
Oxygen										
Ethylene										
Ammonia	0.2944		0.2944						99	88
Lime										
Phosphoric acid										
Sodium hydroxide										
Propylene				0.0981					95	100
Chlorine										
Sodium carbonate										
Urea										
Nitric acid	0.0013								95	99
Ethylene dichloride				0.0108					99	95
Ammonium nitrate										
Vinyl chloride				0.0441			0.0441		98	95
Benzene									N/A	N/A
Ethylbenzene		0.0042		0.0042					99	99
MTBE	0.0012						0.0012	0.0012	100	99
Carbon dioxide										
Styrene						0.0200		0.0200	90	100
Methanol	0.0367		0.0367						99	99
Formaldehyde	0.0061			0.0061					91	100
Xylene									N/A	N/A
Toluene									N/A	N/A
Hydrochloric acid										
p-Xylene		0.0936							70	100
Terephthalic acid			0.0078	0.0078					90	95
Ethylene oxide				0.0289	0.0289		0.0289		80	95
Ethylene glycol									99	99
Ammonium sulfate										
Cumene				0.0034					99	98
Potash										
Phenol				0.0124					97	100
Acetic acid		0.0018		0.0018					99	100
Butadiene				0.0806	0.0806		0.0806		90	75
Carbon black										
Acrylonitrile				0.0235					66.5	100
Propylene oxide				0.0155					90	100
Vinyl acetate				0.0157			0.0157	0.0157	90	100
Titanium dioxide										
Acetone				0.0081					90	98
Cyclohexane							0.0001		100	99.8
Aluminum sulfate										
Sodium silicate										
Adipic acid				0.0204			0.0204		90	100
Calcium chloride										
Caprolactam				0.0011					95	95
Sodium sulfate										
Isobutylene				0.0003	0.0003	0.0003			99	99
Sum	0.339690453	0.100466834	0.33894775	0.3829266	0.109903464	0.020362	0.191026	0.03694	1.52	
normalized fraction	0.223442656	0.06608539	0.22295412	0.25188267	0.072292647	0.013394	0.125654	0.0243		
%	22.34	6.61	22.30	25.19	7.23	1.34	12.57	2.43		

Chemical	Process energy (Btu/lb)	feedstock energy (Btu/lb)	xs feedstock energy (avoids double counting) Btu/lb	feedstock energy (w/o double counting) Btu/lb	fractional savings from overall process improvement	Btu savings in process energy from overall improvement	Btu savings in feedstock energy from overall improvement	New process energy for yield efficient process (Btu/lb)	New process E x production rate (Q/yr)	Process E saved from improving YPP (Q/yr)	Sum of wasted energy from process inefficiencies and extra feedstock use (Q/yr)
Sulfuric acid	840		0	0	0.0080	0.0006	0.0000	833.24	0.0740	0.0002	0.0008
Nitrogen											
Oxygen											
Ethylene											
Ammonia	8000	10500	0	10500	0.1478	0.0425	0.0558	6817.26	0.2451	0.1961	0.2944
Lime											
Phosphoric acid											
Sodium hydroxide											
Propylene	7500	21000	0	21000	0.0526	0.0089	0.0250	7105.26	0.1606	0.0642	0.0981
Chlorine											
Sodium carbonate											
Urea											
Nitric acid	1120		0	0	0.0633	0.0011	0.0000	1049.14	0.0169	0.0002	0.0013
Ethylene dichloride	1700	7800	0	7800	0.0633	0.0017	0.0079	1592.45	0.0254	0.0013	0.0108
Ammonium nitrate											
Vinyl chloride	7500		0	0	0.0741	0.0074	0.0000	6944.15	0.0919	0.0367	0.0441
Benzene	1000	18000	0	18000							0.0000
Ethylbenzene	600	18000	0	18000	0.0203	0.0001	0.0040	587.82	0.0065	0.0001	0.0042
MTBE	5600	21000	21000	0	0.0101	0.0006	0.0000	5543.43	0.0602	0.0006	0.0012
Carbon dioxide											
Styrene	5500	18500	17018.15	1481.85	0.1111	0.0055	0.0015	4888.89	0.0437	0.0131	0.0200
Methanol	4250	12200	0	12200	0.0203	0.0008	0.0022	4163.71	0.0363	0.0338	0.0367
Formaldehyde	0	19000	10228.9	8771.1	0.0989	0.0000	0.0061	0.00	0.0000	0.0000	0.0061
Xylene	4400	18500	0	18500							0.0000
Toluene	4400	18250	0	18250							0.0000
Hydrochloric acid											
p-Xylene	9600	18500	0	18500	0.4286	0.0233	0.0449	5485.71	0.0310	0.0255	0.0936
Terephthalic acid	5500	18500	18500	0	0.1696	0.0053	0.0000	4567.25	0.0258	0.0026	0.0078
Ethylene oxide	170	16000	0	16000	0.3158	0.0003	0.0281	116.32	0.0006	0.0005	0.0289
Ethylene glycol	5600	9100	9100	0	0.0203	0.0006	0.0000	5486.30	0.0281	0.0003	0.0009
Ammonium sulfate											
Cumene	1025	20060	0	20060	0.0307	0.0001	0.0028	993.52	0.0045	0.0004	0.0034
Potash											
Phenol	6500	18700	18696.26	3.74	0.0309	0.0007	0.0000	6298.97	0.0234	0.0117	0.0124
Acetic acid	4600	8300	8300	0	0.0101	0.0002	0.0000	4553.54	0.0164	0.0016	0.0018
Butadiene	22000	24750	0	24750	0.4815	0.0337	0.0379	11407.41	0.0363	0.0091	0.0806
Carbon black											
Acrylonitrile	2600	28000	14246.4	13753.6	0.5038	0.0037	0.0196	1290.23	0.0037	0.0002	0.0235
Propylene oxide	7000	21000	19950	1050	0.1111	0.0021	0.0003	6222.22	0.0168	0.0131	0.0155
Vinyl acetate	6650	12830	11675.3	1154.7	0.1111	0.0020	0.0003	5911.11	0.0157	0.0134	0.0157
Titanium dioxide											
Acetone	5630	15800	14406.44	1393.56	0.1338	0.0018	0.0004	4876.78	0.0117	0.0058	0.0081
Cyclohexane	340	17100	0	17100	0.0020	0.0000	0.0001	339.32	0.0007	0.0000	0.0001
Aluminum sulfate											
Sodium silicate											
Adipic acid	12500	16000	13784	2216	0.1111	0.0024	0.0004	11111.11	0.0194	0.0175	0.0204
Calcium chloride											
Caprolactam	3400	16000	13392	2608	0.1080	0.0005	0.0004	3032.69	0.0042	0.0002	0.0011
Sodium sulfate											
Isobutylene		12000	0	12000	0.0203	0.0000	0.0003	0.00	0.0000	0.0000	0.0003
Sum						0.1459	0.2380			0.4482	0.8320
normalized fraction						0.1753531	0.28600424			0.538643	
%						17.54	28.60			53.86	

Chemical	% used to produce top 12 polymers	Total energy savings for polymer precursors (Q/yr)	Wasted feedstock (bil \$) on polymer precursors	Lbs of CO2 produced on polymer precursors
Sulfuric acid		0	0	0
Nitrogen		0	0	0
Oxygen		0	0	0
Ethylene	81	0	0	0
Ammonia		0	0	0
Lime		0	0	0
Phosphoric acid		0	0	0
Sodium hydroxide		0	0	0
Propylene	46	0.045140526	0	0
Chlorine	30	0	0	0
Sodium carbonate		0	0	0
Urea	6	0	0	0
Nitric acid	10	0.000130807	0.003575	0
Ethylene dichloride	88	0.00954737	0.0643104	0.72248
Ammonium nitrate		0	0	0
Vinyl chloride	84	0.037045989	0.2217684	1.16004
Benzene	64	0	0	0
Ethylbenzene		0	0	0
MTBE		0	0	0
Carbon dioxide		0	0	0
Styrene	77	0.015436424	0.1438668	1.76946
Methanol	27	0.009914552	0	0.05751
Formaldehyde	29	0.001755936	0.014577952	0.3132
Xylene		0	0	0
Toluene	4	0	0	0
Hydrochloric acid		0	0	0
p-Xylene	100	0.093622869	0.133719	0
Terephthalic acid	99	0.007758265	0.067716	0.62271
Ethylene oxide	28	0.008103431	0.0875728	0.98336
Ethylene glycol	29	0.000250286	0.0053505	0.02378
Ammonium sulfate		0	0	0
Cumene	63	0.002122038	0	0
Potash		0	0	0
Phenol	54	0.006712654	0.015768	0.26082
Acetic acid		0	0	0
Butadiene	16	0.012903733	0.0660608	0.7984
Carbon black		0	0	0
Acrylonitrile	18	0.004229442	0.0261927	0.29322
Propylene oxide	17	0.00263823	0.008208025	0.27081
Vinyl acetate		0	0	0
Titanium dioxide		0	0	0
Acetone		0	0	0
Cyclohexane	82	6.94853E-05	0.000468384	0.01148
Aluminum sulfate		0	0	0
Sodium silicate		0	0	0
Adipic acid	74	0.015067469	0.01495984	0.26048
Calcium chloride		0	0	0
Caprolactam	87	0.000961318	0.0819279	0.30276
Sodium sulfate		0	0	0
Isobutylene		0	0	0
Sum		0.273410824	0.956042501	7.85051
normalized fraction				
%		32.86	47.29	37.56

APPENDIX II

Calculation of Excess Feedstock Required and Carbon Dioxide Generated

(attached file: waste1.xls)

Chemical	Production lb (bil) 92	Process	Feedstock	Total Feedstock Conversion %	Product yield Mol%	Biprodukt Yield Mol%	Feedstock Waste -- lb (bil)	Feedstock unit cost \$/lb
Sulfuric acid	88.8	catalytic conversion	SO2	99.70%	99.20%	0.00%	.467	.115
Nitrogen	58.7		air	Not Specified	N/A	0.00%	NA	NA
Oxygen	42.38							
Ethylene	40.41							
Ammonia	35.95	ammonia synthesis	hydrogen	88.00%	87.12%	0.00%	.625	
			air (N2)	NA	NA	NA	NA	NA
Lime	34.72							
Phosphoric acid	25.36							
Sodium hydroxide	24.02							
Propylene	22.6	Catalytic reforming	ethane	95.00%	1.71%	93.29%	.000	
Chlorine	22.28							
Sodium carbonate	20.89							
Urea	16.84							
Nitric acid	16.08	Oxidation	ammonia	99.00%	94.05%	0.00%	.275	.130
			air (oxygen)	90.00%	NA	NA	NA	NA
Ethylene dichloride	15.94	Oxychlorination	ethylene	95.00%	94.05%	0.50%	.261	.280
			chlorine	100.00%				.108
Ammonium nitrate	15.33							
Vinyl chloride	13.23	thermal decomposition	ethylene dichloride	95.00%	93.10%	0.00%	1.553	.170
Benzene	12.01	Catalytic reforming	naphtha	NA	NA	NA	NA	.148
Ethylbenzene	10.99	Alkylation	ethylene	99.00%	98.01%	1.00%	.029	.280
			benzene	100.00%	98.01%		.164	.143
MTBE	10.86	Reactive distillation	methanol	99.00%	99.00%	0.00%	.096	.068
			isobutylene	100.00%	99.00%	1.00%	.000	.310
Carbon dioxide	10.79							
Styrene	8.94	Dehydrogenation	ethylbenzene	100.00%	90.00%	3.15%	.693	.270
Methanol	8.73	Methanol synthesis	carbon monoxide	99.00%	98.01%	0.00%	.155	
			hydrogen	not specified	not specified	not specified	not specified	
Formaldehyde	6.98	Dehydrogenation	methanol	100.00%	91.00%	0.00%	.736	.068
			air (oxygen)	100.00%	NA	0.00%	NA	NA
Xylene	6.38	Catalytic reforming	naphtha	NA	NA	NA	NA	.148
Toluene	6.03	Catalytic reforming	naphtha	NA	NA	NA	NA	.148
Hydrochloric acid	5.75							
p-Xylene	5.66	isomerization	mixed xylenes and ethylbenzene	100.00%	70.00%	19.60%	.841	.159
Terephthalic acid	5.64	Air oxidation	p-xylene	95.00%		0.00%	.190	.360
			air	100.00%	NA	NA	NA	NA
Ethylene oxide	5.56	Oxidation (epoxidation)	ethylene	95.00%	76.00%	0.00%	1.117	.280
			oxygen	100.00%	NA	NA	NA	
Ethylene glycol	5.12	Hydration	ethylene oxide	99.00%	89.10%	9.90%	.041	.450
			water	NA	NA	NA	NA	NA
Ammonium sulfate	4.72							
Cumene	4.57	alkylation	benzene	98.00%	97.02%	2.98%	.000	.143

Chemical	Production lb (bil) 92	Process	Feedstock	Total Feedstock Conversion %	Product yield Mol%	Biproduct Yield Mol%	Feedstock Waste -- lb (bil)	Feedstock unit cost \$/lb
			propylene	100.00%	92.00%	8.00%	.000	.223
Potash	3.76							
Phenol	3.71	cumene peroxidation	cumene	100.00%	97.00%	0.00%	.146	.200
			air	100.00%	NA	NA	NA	NA
Acetic acid	3.6	methanol carbonylation	methanol	100.00%	99.00%	0.00%	.027	.068
			carbon monoxide	90.00%	89.10%	0.00%	.206	
Butadiene	3.18	oxidative dehydrogenation	mixed linear butenes	75.00%	67.50%	0.00%	1.588	.260
			Steam	Not Specified	Not Specified	none	Not Specified	NA
Carbon black	3.02							
Acrylonitrile	2.83	ammoxidation (oxidative amination)	propylene	100.00%	66.50%	14.10%	.654	.223
			ammonia	Not specified	Not specified	Not specified	Not specified	.130
			air	Not specified	Not specified	Not specified	Not specified	NA
Propylene oxide	2.7	peroxidation	propylene	100.00%	90.00%	0.00%	.217	.223
			isobutane (ethylbenzene)	100.00%	90.00%	0.00%	.300	
			oxygen	100.00%	90.00%	0.00%	.166	
Vinyl acetate	2.66	catalytic oxidation	ethylene	100.00%	90.00%	0.00%	.096	.280
			acetic acid	100.00%	100.00%	0.00%	.000	.330
			oxygen	100.00%	90.00%	0.00%	.110	
Titanium dioxide	2.53							
Acetone	2.39	cumene peroxidation	cumene	NA	NA	NA	NA	.200
			air	NA	NA	NA	NA	NA
Cyclohexane	2.21	hydrogenation	benzene	99.80%	99.80%	0.00%	.004	.143
			hydrogen	92.40%	92.40%	0.00%	.004	
Aluminum sulfate	2.18							
Sodium silicate	1.8							
Adipic acid	1.75	catalytic oxidation	cyclohexane	100.00%	90.00%	0.00%	.112	.181
			nitric acid	Not specified	Not specified	0.00%	Not specified	.183
			air	100.00%	Not specified	0.00%	Not specified	NA
Calcium chloride	1.39							
Caprolactam	1.38	Beckman rearrangement	cyclohexanone	95.00%	90.25%	0.00%	.129	.730
			hydroxylamine	Not specified	Not specified	Not specified	Not specified	NA
Sodium sulfate	1.34							
Isobutylene	1.29	dehydrogenation, isomerization	n-butanes	99.00%	98.01%	0.00%	.027	.260
Sum	655.98						11.030	

Chemical	Feedstock Waste \$1billion	No-value Hydrocarbon Co- and byproducts	Feedstock Waste CO2 Equivalent	Valuable Co- and Byproducts	Other Notes	References
Sulfuric acid	.054	none	.000	none		
	NA	NA	.000	none		
Nitrogen						
Oxygen						
Ethylene						
Ammonia	.000	none	.000	none		
	NA	none	NA	NA		
Lime						
Phosphoric acid						
Sodium hydroxide						
Propylene	.000	0	.000	Other hydrocarbon fractions		Hatch and Matar 1981, p. 74
Chlorine						
Sodium carbonate						
Urea						
Nitric acid	.036	none	.000	none		
	NA	none	NA	NA		
Ethylene dichloride	.073	C1 and C2 carbon oxides and chlorides	.821	none		McKetta, 1984, V. 20, p. 213
	.000					
Ammonium nitrate						
Vinyl chloride	.264	chlorinated carbons	1.381			
Benzene	NA	NA	NA	Other hydrocarbon fractions		
Ethylbenzene	.008	none	.092	polyethylbenzenes		Hatch and Matar, p. 138
	.023		.556			
MTBE	.007	methanol purge	.096	(unreactive C4 hydrocarbons added with feed)	unreacted MeOH, and C4 hydrocarbons allowed in gasoline product	Hatch and Matar 1981, p. 128
	.000	none	.000	t-butyl alcohol, diisobutylene	biproducs can be used in gasoline	HP 1995, p. 112; Chemical Engineering 1979, p. 209
Carbon dioxide						
Styrene	.187	tar, CO, CO2	2.302	Toluene (.031kg/kg styrene)		Hatch and Matar 1981, p. 138, Chemical Engineering, 1079, p. 269, Lowenheim and Moran, 1975, p. 782
Methanol	.000	ethers, esters, acetone, hydrocarbons, higher alcohols	.213	none		
	NA	NA	.000	none		
Formaldehyde	.050	carbon dioxide	1.080	none		
	NA	NA	NA	none		
Xylene	NA	NA	NA	Other Hydrocarbons		
Toluene	NA	NA	NA	Other Hydrocarbons		
Hydrochloric acid						
p-Xylene	.134	m-xylene	.000	C7- hydrocarbons and C9+ aromatics	HP 1995 indicates 87 - 95% selectivity at 30% conv./pass; 70% overall yield of p-xylene with 19.6% o-xylene coproduced.	HP1995, p. 149 Pearce and Patterson 1981, p. 210-12
Terephthalic acid	.068	4-carboxy benzaldehyde	.629	none	90% selectivity at 95% conversion	Pearce and Patterson 1981, p. 284
	NA	none	NA	none		
Ethylene oxide	.313	CO2	3.512			
	NA	none	NA	none		
Ethylene glycol	.018	not specified	.082	diethylene glycol, triethylene glycol	Yield >99.5; 102 lb diethylene- and 5 lb triethylene-glycols/1000 lb ethylene glycol	Chemical engineering
	NA	NA	NA	NA		
Ammonium sulfate						
Cumene	.000	none	.000	polyalkylated benzenes		Lowenheim and Moran 1975, p. 295

Chemical	Feedstock Waste \$1billion	No-value Hydrocarbon Co- and byproducts	Feedstock Waste CO2 Equivalent	Valuable Co- and Byproducts	Other Notes	References
Potash	.000	none	.000	polyalkylated benzenes	reacted with balance used in making heavier aromatics	Chenier 1986, p. 178 Chemical Engineering 1979, p. 152-4
Phenol	.029 NA	tars none	.483 0.00%	NA	97% achievable by hydrogenating a-methylstyrene to cumene and recycling.	HP 1995, p. 133
Acetic acid	.002 .000	propionic acid, flare gas NA	.027 .323	none none		Moran and Lowenheim 1975, p. 10 Leach 1983, p. 278
Butadiene	.413 NA	vinylacetylene, formaldehyde, acetaldehyde, acrolein NA	4.990 0	none none		
Carbon black						
Acrylonitrile	.146 NA NA	CO, CO2, acrolein NA NA	1.629 .000 .000	acetonitrile, hydrogen cyanide acetonitrile, hydrogen cyanide NA	One kg propylene yields 0.84 kg acrylonitrile, 0.03 kg acetonitrile and 0.13 kg hydrogen cyanide	Lowenheim and Moran, 1975, p. 46-7
Propylene oxide	.048 .000 .000	Not specified Not specified Not specified	.683 .910 .000	Tert-butyl alcohol (to make isobutylene or MTBE) [a-phenylethyl alcohol (to make styrene)] NA NA	93% yield; 2.2 kg t-butyl alcohol/kg propylene oxide	Lowenheim and Moran 1975, p. 695
Vinyl acetate	.027 .000 .000	CO2, acetaldehyde none none	.302 .000 .000	none none none		Pearce and Patterson 1981, p. 270
Titanium dioxide						
Acetone	NA NA	NA NA	NA NA	NA NA	coproduct of phenol production from cumene	
Cyclohexane	.001	unreacted benzene NA	.014 .000	none none		McKetta 1982, vol 14, p. 70-1, 76-7
Aluminum sulfate						
Sodium silicate						
Adipic acid	.020 NA NA	esters and ethers, dicarboxylic acids, glutaric and succinic acids NA NA	.352 .000 .000	none none none	90 - 96% yield	Lowenheim and Moran 1975, p. 52; Kirk Othmer 1991, vol. 1, P. 476-80
Calcium chloride						
Caprolactam	.094 NA	not specified NA	.348 .000	Ammonium sulfate, Hydrogen NA	1.750 lb NH3SO4/lb caprolactam, .021 lb H2/lb caprolactam	Chemical Engineering 1979, p. 138
Sodium sulfate						
Isobutylene	.007	none	.082	Hydrogen	89% isobutylene yield, 2.5-3% hydrogen yield	HP 1995, p. 104
Sum	2.022		20.907			

APPENDIX III

Process Information and Limitations

(attached file: top50proc_ref.xls)

Chemical	Subprocess	Feedstock	Operating conditions	Catalysts	Notes
Sulfuric acid	Catalytic converter	SO ₂ , air	T(inlet) = 450 C T(max) = 500 - 600 C, T(exit) = 420 - 450 C	6 - 10% V ₂ O ₅ with K promoter on Silica	99.7 - 99.9% conversion achieved in a single pass with two stages separated by a acid removal stage. Reaction is negligible below 400 .
Nitrogen					
Oxygen					
Ethylene					
Ammonia	Primary reformer	Methane or naptha, stream	T (exit) < 700 - 750 C, P= 30-40 bar	Nickel	Pressure set high to reduce subsequent processing costs. Temp set to achieve rapid kinetics and favorable equilibrium conditions. Approx. 70% conversion of CH ₄ .
	Secondary reforming	Primary reformer product, air (H/N = 3/1)	T (exit) < 900 C, P = 30 - 40 bar	14% Ni 15% CaO 67% Al ₂ O ₃	Pressure set high to reduce subsequent processing costs. Temp set to achieve rapid kinetics and favorable equilibrium conditions. Methane reduced to 0.2 - 0.25%.
	Water gas shift	Secondary reformer product	HT shift: T (exit) = 825 C LT Shift: T (exit) = 350 - 650 C	HT: 55% Fe 6% Cr LT: 32 - 62% ZnO 15 - 31% CuO 0 - 40.5% Al ₂ O ₃	Process is reaction rate limited, but high temp favors CO in product stream which is not desired
	Ammonia Synthesis	water gas shift product after CO ₂ and O ₂ removal	T(max) = 510 C, P = 80 - 110 bar	93% Fe ₂ O ₃ 3.3% Al ₂ O ₃ 0.67% MgO 0.55% SiO ₂ 3.0% CaO 0.65% K ₂ O	Process is reaction rate limited due to catalyst deactivation (sintering at higher temp and gradual poisoning), and equilibrium limited that is favored at lower temp. Process is exothermic causing potential hotspots. Get 10 - 20% conversion/pass.
Lime					
Phosphoric acid					
Sodium hydroxide					
Propylene	Cracking, steam cracking	Ethane, Naptha, gas oil, resid oil, crude petroleum, other refinery gases	Ethane T = 750- 850 C, P = 1 - 1.25 atm, Steam diluent = 0 - 50% Naptha T = 840 C, P = 1+ atm, Steam Dil. = 60%, t(res) = 0.35 sec.	None	Propylene produced mainly by steam cracking of hydrocarbons. Ethane conversion/pass = 60% , propylene yield = 1.8%, Propylene yield from naptha = approx 12 - 16% (single pass).
	metathesis	ethylene and butene	Not specified	Not identified	Overall conversion of butenes to 78 - 92% as the n-butenes content of feed increases from 78% to 92%
	dehydrogenation	propane	T = 537 - 649 C P = 5 - 20 in. Hg	CATOFIN (Base metal)	55 - 60% conversion/pass, 92% selectivity, 85 -90 wt% yield
Chlorine					
Sodium carbonate					
Urea					
Nitric acid	Catalytic Combustion	NH ₃ , air	T = 820 - 950 C P = 1 - 12 Bar t(res) = 0.001 sec	Platinum alloy gauze containing 5 - 10%Rh or optionally 5% Pd and 5% RH	Considered one of the most efficient catalytic process. 94% yield at 10 bar (to 98% at 1 bar). Favored by high temp low press. High press proc pref. to reduce NOX emmissions; but cat life limited at higher required temp.
Ethylene dichloride	Balanced oxychlorination - Direct chlorination step	Ethylene, Chlorine	Liquid Phase P = 1 - 10 bar Ethylene Bromide cat T - 40 - 50 C Iron(III) Chloride cat. T = 53 -65 or 109 C Vapor phase 370 - 500 C	Ethylene Bromide Iron(III) Chloride	Exothermic. 90+% yield conversion/pass in the 90s 99.8% purity

Chemical	Subprocess	Feedstock	Operating conditions	Catalysts	Notes
	Balanced oxychlorination - oxychlorination step	Ethylene, HCl, air/O ₂	T = 225 - 315 C	Modified decontype (Copper Chloride on alumina; KCL, rare earth chloride?)	Exothermic
Ammonium nitrate					
Vinyl chloride	Pyrolysis	Ethylene dichloride	T = 430 - 530 C P = 10 - 35 Bar	Pumice or Charcoal	50 - 60% conversion. 95% selectivity
Benzene	Catalytic Reforming (hydroforming, platforming, rheniforming)	Naptha (cyclohexane, methyl cyclopentane)	Pt Catalyst T = 450-510 C P = 250 - 800 psi Pt/Rh Catalyst t = 480 - 540 C P = 100 - 200 psig	Platinum metal on alumina support, Pt,-Rh	Endothermic reaction req. interstage heating 80% yield/pass from C6 naphthenes+ 1 - 9% in feed, Gross yld of aromatics = 90 - 95% of theoretical. Higher ylds from Pt/Rh cat. (High temp/ Lower press) Cats. sulfur sensitive, deactivate faster at low P.
	Hydrodealkylation	Toluene or toulene rich feedstocks, hydrogen	T = 550 - 650 C p = 375 - 750 psi	Ni, Cr, Mo or Co supported on alumina or Silica-alumina	Exothermic Rx. 96+% yield. Some hydrocracking occurs producing C1 to C6 Paraffins. some biphenyl and polycyclics produced.
	Hydrodealkylation	Toluene, steam	T = 600 - 800 (most cat.) T = 320 - 630 (Ni on Al ₂ O ₃)	Y, La, Ce, Pr, Nd, Sm, Th compounds: Nickel on alumina	90% yields
	disproportionation	Toluene	Co-Mo cat. T = 450 - 530 C P = 300 Psig ZMS-5 Zeolite T = 480	ZMS-5 Zeolite CoO-MoO ₃ on aluminosilicat/alumina	40% conversion/pass, 97% yield. Equilibrium limited to 58% conversion, Conversion > 40% produces more side Rx. and catalyst deact.
Ethylbenzene	Liquid phase alkylation	Benzene (styrene grade), ethylene	T = 40 - 100 C C P = 30 - 100 psi	Aluminum chloride-hydrogen chloride-hydrocarbon complex	90-99+ overall yld. Approx. 70% sel. over polyethylbenzene (PEB) in .proc. Used in styrene syn. proc. Friedle-Crafts Alkylation. Excess Benzene to min. PEB biprod. that is recycled and conv. to ethylbenze in reactor. 100% conv. ethylene/pass
	Vapor phase alkylation	Benzene, ethylene	T = 150 - 250 C P = 400 - 700 psi	Boron trifluoride	99+% yield. Multiple pass. Designed to used high ethylene (8 - 10%) refinery gas as feedstock. Up to 5 - 100% ethylene can be used.
	Mobil Badger Process	Ethylene, Benzene (makeup) most benzene may be a recycled intermediate in the process	T = 370 - 420 C P = 200 - 400 psig	Crystalline aluminosilicate zeolite (ZSM-5)	Benzene/Ethylene = 7.5/1 (5/1 - 20/1)
	High Temperature Process	98% Ethylene?	T = 260 C P = 900 - 950 psig	solid phosphoric acid	None
MTBE		Methanol, Isobutylene	T(inlet) = 25 C T(outlet) = 90 C P > 1atm to maintane liquid phase	acidic ion-exchange resin such as ssulfonated polystyrene cross-linked with divinyl benzene (Amberlist 15)	Equil. limited. Temp maint. below 90 C to improve equil. and extend cat life. Cat. very specific to Isobutylene in C4 mixture. Butadiene polymerzizes. Water reacts with isobutylene to make isobutyl alcohol. 90-96% MEOH conv./pass. 99+% propylene/pass
Carbon dioxide					

Chemical	Subprocess	Feedstock	Operating conditions	Catalysts	Notes
Styrene	Catalytic dehydrogenation	Ethylbenzene	T = 600 - 700 C P = 1 atm (res) = 1 sec.	Fe-Cr Oxides (also Fe ₂ O ₃ , SiO ₂ , Al ₂ O ₃ , solid phosphoric Acid, Cobalt Oxides, and ZnO promoted with Alumina and chromates). Diffusion limit in catalyst. Want to min. press. drop. heating. Equilibrium process. adiabatic beds with interstage conv./pass. 90% yield. 2 Endothermic Rx. 30 - 60% conv./pass. 90% yield. 2	polymerization. bed. Sulfur added to minimize
	Peroxidation	ethylbenzene, oxygen, propylene	T = 80 - 130 C P = 550 psig, Coprod. a-phenylethyl alcohol converted to styrene	Mo compounds (coordination compounds of Molybdenum hexacarbonyl and propylene oxide. 10 - 22% conversion of Propylene/pass.	Propylene conversion to -oxide- 22%, sel. - 95%+. Hydroperoxide - 98% conv., 80 - 90% Sel. Noncat. conv. of Ethylbenzene and air to hydroperoxide. Propylene oxide coprod. 2.5 kg of styrene/kg
Methanol	Carbon monoxide (and some carbon dioxide), Hydrogen	MeOH synthesis loop	T = 240 - 270 C P = 725 - 1500 psi	CuO/ZnO on alumina, CuO/ZnO composite	About 5% - 6% (vol.) of methanol produced per pass. Equilibrium limited (favored low temp. High pressure to achieve acceptable reaction rate.
Formaldehyde	dehydrogenation	Methanol, air	Silver Catalyzed T = 450 - 650 C (635 C pref) P = 1 atm, (T res) = 0.01 sec, [MeOH] > 36.5% Iron molybdate Catalyzed T < 430 C, P = 1 atm (T res) = 0.3 sec, [MeOH] < 6.7%	Silver as gauze, crystals or granules Fe(MoO ₄) ₃ and MoO ₃ mixture	Ag process selectivity is 85 - 90%, conversion is 60 - 73%. FeMo process selectivity is 91 - 94%, conversion is 99%. Feed constraints limited by explosive limits for MeOH, FeMo cat. sublimates above 400 C. Air addition eliminates Equil. const.
Xylene	Catalytic Reforming (hydroforming, platforming, rheniforming)	Naphta (cyclohexane, methyl cyclopentane), hydrogen	Pt Catalyst T = 450-510 C P = 250 - 800 psi P/RH Catalyst T = 480 - 540 C P = 100 - 200 psig	Platinum metal on alumina support, Pt-Rh	Endothermic reaction req. interstage heating 80% yield/pass from C ₆ naphthenes + 1 aromatics = 90 - 95% of - 9% in feed, Gross yld of theoretical. Higher ylds from P/RH cal. (High temp/ Lower press) Cats. sulfur sensitive, deactivate faster at low P.
	disproportionation	Toluene	Pt Catalyst T = 450-510 C P = 250 - 800 psi P/RH Catalyst T = 480 - 540 C P = 100 - 200 psig	Platinum metal on alumina support, Pt-Rh	Endothermic reaction req. interstage heating 80 - 90% conversion. May use 1 or 2 passes in Rx. Cats. sulfur sensitive, deactivate faster at low P.
	Catalytic Reforming (hydroforming, platforming, rheniforming)	Naphta (dimethylcyclohexane, ethylcyclopentan), hydrogen	Pt Catalyst T = 450-510 C P = 250 - 800 psi P/RH Catalyst T = 480 - 540 C P = 100 - 200 psig	Platinum metal on alumina support, Pt-Rh	Endothermic reaction req. interstage heating 80 - 90% conversion. May use 1 or 2 passes in Rx. Cats. sulfur sensitive, deactivate faster at low P.
Toluene	Catalytic Reforming (hydroforming, platforming)	Naphta (dimethylcyclohexane, ethylcyclopentan), hydrogen	Pt Catalyst T = 450-510 C P = 250 - 800 psi P/RH Catalyst T = 480 - 540 C P = 100 - 200 psig	Platinum metal on alumina support, Pt-Rh	Endothermic reaction req. interstage heating 80 - 90% conversion. May use 1 or 2 passes in Rx. Cats. sulfur sensitive, deactivate faster at low P.
Hydrochloric acid					
p-Xylene	disproportionation	Toluene, hydrogen (recycle gas)	Moderate T and P	Proprietary Mobil Catalyst	30% toluene conversion/pass, 87 Equilibrium limited, not effected by T. Catalyst type selected for ability to convert ethylbenzene in feed to xylenes. Zeolite pore structure affects by-product dist. and purity req. of feed.
	Isomerization	Mixed xylenes/ethylbenzene	T = 430 - 480 C P = 10 - 20 atm	ZSM-5 Zeolite (Mobil) Borosilicate molecular sieve (Amoco)	

Chemical	Subprocess	Feedstock	Operating conditions	Catalysts	Notes
Terephthalic acid	air oxidation	p-xylene, air	Br salt promoted; T = 200C, P = 225-400 psi Acetaldehyde promoted T = 120 - 175 C P = 100 - 200 psig MEK promoted T = 95 - 150 C, P = 5-150 psig	cobalt and manganese salts of heavy metal bromides	99.6% purity and 90 - 95% yield (90% sel. at 95% yld). Acetic acid used as solvent in Proc. Purity improved by hydrogenation of formylbenzoic acid impurity to p-methylbenzoic acid and crystallization. 99.9% pure product
	disproportionation	Potassium benzoate,	liquid phase CO ₂ at 740 psi	Zn and Cd compounds (CdO)	Reaction takes place in CO ₂ atm.
Ethylene oxide	oxidation (epoxidation)	Ethylene, air, oxygen	T = 260 - 280 C (air) T = 230 C (oxygen) P = 1 - 3 MPa t(res) = 1 sec.	Silver, with trace of Cs	10 - 15% conversion/pass. 88 - 94% selectivity reported using alkali metal cations in, on or under silver particles on alumina. Carbon dioxide inhibits Rx. removed in an absorber before stream recycle. Lower temp. favors selectivity and conversion.
Ethylene glycol Ammonium sulfate	Hydration	Ethylene oxide, water	T = 50 - 100 C t(res) = 30 min. Ethylene/water = 10/1	0.5 - 1.0% H ₂ SO ₄	100% yield of products with about 10% of product di- and triethylene glycol ethers
Cumene Potash	Alkylation	Benzene, Propylene	T = 200 - 250 C P = 400 - 600 psi	H ₂ PO ₄ on kieselguhr	96 - 97% yield on Benzene. 91 - 92% yield on propylene. Excess benzene used to minimize diisopropylene benzene formation which must further react with benzene to produce cumene in a separate step. Cat. distillation process recently demonstrated.
Phenol	Cumene Peroxidation	Cumene, air	Peroxidation T = 100 - 130 C (130 - 140 C) P = 25 - psig (20 - 250 psi) Decomposition T = 60 - 80 C P = 5 psig t(res) = 15 min.	Peroxidation - metal salts (?) decomposition - mineral acid (H ⁺)	30 - 50% conversion/pass and 85 - 95% yield of cumene hydroperoxide intermediate. 90 - 95% yield of phenol from hydroperoxide intermediate. 90 - 98% overall yield. Exothermic. 91 - 93% overall yield of acetone coproduct. Other byproducts made.
Acetic acid	Acetaldehyde oxidation	Ethylene, Oxygen (air) (acetaldehyde is an intermediate product in integrated system)	Ethylene oxidation T = 130 C P = 45 psig Acetaldehyde oxidation T = 66 C P = liquid phase (about 15 psi - 75psi)	Ethylene Oxidation - CuCl ₂ and PdCl ₂ Acetaldehyde oxidation - Mn(OAc) ₂ or Co(OAc) ₂	95% yield of Acetaldehyde from ethylene. 95% yield of acetic acid from acetaldehyde with up to 50% conversion/pass. Homogeneous cat.
	n-butane oxidation	95% n-butane (2.5% isobutane, 2.5% pentane), air (air/butane = 5/1), Europe uses pentane and hexane feedstocks	T = 50 - 250 C P = 800 psi	Cobalt, manganese or chromium acetate	75 - 80% selectivity (6% formic acid, 6% ethanol, 4% methanol, 4 - 9% other). Homogeneous cat. Process conditions can be modified to emphasize formic acid or MEK production at expense of acetic acid.
	Methanol Carbonylation	methanol, CO	T = 150 - 200 C (175 C) P = 100 - 215 atm. (1 atm)	Rhodium and iodine catalyst system	99+% yield based on methanol, 90+% yield based on CO. +Leach 1983 gives good discussion of catalytic Rx.

Chemical	Subprocess	Feedstock	Operating conditions	Catalysts	Notes
Butadiene	Oxidative dehydrogenation of Butenes	Mixture of linear Butenes, steam	T(inlet) = 340 - 360 C T(outlet) = 575-595 C 1 atm t(res) = 0.2 sec steam/feedstock = 10/1	Iron spinel - Zn(Cr(1-x)Fe(x))O ₄ or Mg(Cr(1-x)Fe(x))O ₄	Yield from butane = 60%. Exothermic, 80 - 93% selectivity, 65 -75% conversion/pass, all O ₂ consumed, 10% loss of carbon as carbon oxides. Catalyst deactivates at > 595 C. stm/butylene ratio = 12/1 to control temp
	Catalytic Dehydrogenation	n-Butanes and n-Butenes	T = 600 - 700 C for rection of Butanes T = 500 - 600 C for reaction of butenes T(res) = 0.2 sec Above 700 C coking is a problem	Chromia alumina Catalyst for butanes, 70% Fe ₂ O ₃ with 27% K ₂ O Promoter and 3% Cr ₂ O ₃ stabilizer used for Butenes	Endothermic. Eq. lim. Cr cat. can't be used with stm as a dil. to improve equil. Yld at 1 atm approx 60%. Fe cat. tolerates stm used to obtain approx. 100% conv. at 0.1Bar. Both proc. are obsolete. Coking a prob. above 700 C, Rate a prob below 600
Carbon black					
Acrylonitrile	Ammoxidation (oxidative amination)	Propylene, NH ₃ , air		Antimony oxide-uranium oxide; Antimony oxide-iron oxide; Ni,Co, Fe, Bi, Mo oxide composite: Te,Ce, Mo oxides on Silica	95% conversion (single pass), 80% selectivity. Acetonitrile and hydrogen cyanide bi-products
Propylene oxide	Chlorohydrin formation	Propylene, Chlorine, 10% Ca(OH) ₂ solution	T = 35 C P = 1 atm	none	Cl ₂ converted to dilute CaCl ₂ . Propylene and Cl ₂ reacted noncatalytically to produce Chlorohydrine and 0.1lb dichloride/lb chlorohydrine. 95% Yield on Chlorohydrine in catalytic step.
	Peroxidation	isobutane, ethylbenzene, or acetaldehyde, isopentane, isopropanol; oxygen, propylene	Isobutane T = 120 - 150 C P = 450 psi Coprod. Tert-butyl alcohol Ethylbenzene T = 80 - 130 C P = 550 psig, Coprod. - styrene	Isobutane - MoNapthenate Ethylbenzene - Mo compounds	Noncatalytic conversion of isobutane etc. to peroxide. Propylene oxide and tert.butyl alcohol etc. coproduct produced 93% of theoretical yield from Isobutane. 2.2 kg of coproduct/kg product. 10 - 22% conversion of Propylene/pass.
Vinyl acetate	catalytic oxidation	Ethylene, acetic acid, oxygen	Vapor phase T = 175 - 200 C P = 25 - 140psig	Pd on alumina or silica alumina or Pd on carbon, plus potassium acetate	Yield 91 - 95% based on ethylene. Conv/pass 10 - 15% on ethylene, 15 - 30% on acetic acid, 60 - 90% on oxygen; 91 - 94% selectivity. Highly exothermic KOAc slowly volatilize. 10% O ₂ at inlet to stay below flammability limit. Rx diffusion. limited.
Titanium dioxide					
Acetone	Cumene Peroxidation	Cumene, air	Peroxidation T = 100 - 130 C (130 - 140 C) P = 25 - psig (20 - 250 psi) Decomposition T = 60 - 80 C P = 5 dpdog	Peroxidation - metal salts (?) decomposition - mineral acid (H+)	30 - 50% conversion/pass and 85 - 95% yield of cumene hydroperoxide intermediate. 90 - 95% yield of phenol from hydroperoxide intermediate. 90 - 98% overall yield. Exothermic. 91 - 93% overall yield of acetone coproduct. Other byproducts made.
	Dehydrogenation	Isopropanol	T = 450 - 550 C P = 40 - 50 psig	Cu, brass or ZnO	95 - 98% yield, up to 98% conversion /pass claimed for one process
	Oxidation-dehydration	Isopropanol, air	T = 400 - 600 C P = 40 - 50 psi	Cu or Ag	85 - 95% yield

Chemical	Subprocess	Feedstock	Operating conditions	Catalysts	Notes
Cyclohexane	Hydrogenation	benzene, hydrogen	Ni on alumina T = 150 - 220 C P = 300 - 450 psi Sulfided nickel or Pd T = 450 C P = 4500 psi	supported Ni, Pd, Pt	99.6% yield. Highly exothermic, several adiabatic beds. Favored by low temp. Isomerization at higher temp. Appears to be a single pass process for benzene. Product recycled to cool reaction.
Aluminum sulfate					
Sodium silicate					
Adipic acid	catalytic oxidation	cyclohexane 98% purity, air and nitric acid	Hexane oxidation T = 125 - 160 C P = 50 - 250 psi Hexanol/Hexone oxidation T = 50 - 90 C p = 1 - 4 atm t(res) = 10 - 30 min	cobalt (II) naphthenate or acetate Second step ammonium vanadate and copper	10% conversion/pass of cyclohexane to cyclohexanol/cyclohexanone intermediate to get a 65% - 90% yield. Boric acid additive improves selectivity to intermediates. Overall yield of adipic acid 90 - 95%. removal of H2O byproduct essential to high yields
	catalytic oxidation	cyclohexane, air	T = 90 C P = liquid phase t(res) - 9 hr in acetic acid	Cobalt acetate	88% overall conversion, 73% yield. Acetic acid is Rx. medium.
Calcium chloride					
Caprolactam	Beckman rearrangement	Cyclohexanone (from cyclohexane [58%] or phenol [42%]), hydroxylamine(made from NH3, CO2, S, air)	T = 100 - 200 C	sulfuric acid	90% yield (single pass). Ammonium sulfate by product produced (phosphoric acid to produce ammonium phosphate also used).
Sodium sulfate					
Isobutylene	Isomerization	n-butanes			90% yield from butane (iso?)
	dehydration	tert-butyl alcohol			Tert. butyl alcohol coproduced with propylene oxide from propylene

Chemical	References	Process limitations	Strategies to overcome limitations	Other process notes
Sulfuric acid	Considine, 1974	Efficient process; one reaction step equilibrium limited	No specific strategies noted	
Nitrogen				
Oxygen				
Ethylene				
Ammonia	HP 1993 Slack and James 1973	Equilibrium-limited reactions	remove H ₂ as formed to improve conversion at lower temp. Improved catalyst activity to reduce Rx. temp.	
	HP 1993 Slack and James 1973	Equilibrium-limited reaction	remove CO, H ₂ as formed to improve conversion at lower temp. Improved catalyst activity to reduce Rx. temp.	
	HP 1993 Slack and James 1973	Slow reaction rates	remove CO ₂ , H ₂ as formed to improve conversion at higher temp	
	HP 1993 Slack and James 1973	Equilibrium-limited reaction; catalyst deactivation; heat removal limited	Better catalyst activity, heat removal not a big problem, Intraparticle mass transfer limits rate, remove NH ₃ as formed to break equilibrium	
Lime				
Phosphoric acid				
Sodium hydroxide				
Propylene	Hatch and Matar 198, p. 74, 77	Produced with other valuable products	No specific Strategies Noted, because multiple coproducts are produced	FCC also produces propylene but at a lower yield, and is considered an undesirable byproduct in gasoline production
	HP 1995, p. 144		Improve conversion of isobutene.	
	HP 1995, p. 144	competing rxns	Improve selectivity of catalyst.	
Chlorine				
Sodium carbonate				
Urea				
Nitric acid	Buchner et. al. 1989, p. 56-67	Equilibrium-limited reaction	No strategy noted. but a more temperature resistant catalyst would improve yield by allowing higher temp. (equilibrium limited)	
Ethylene dichloride	Hatch and Matar 1981, p. 97 Lowenheim and Moran 1975, p. 392-3 Satterfield 1991, p. 304-5 HP., 1995, p. 148 Pearce and Patterson, 1981, p. 281-91	competing rxns	Pearce and Patterson suggests improved oxychlorination catalysts to complete reaction without HCL production, and oxychlorination of ethane.	Heat removal is important to prevent possible explosions.

Chemical	References	Process limitations	Strategies to overcome limitations	Other process notes
	Hatch and Matar 1981 Lowenheim and Moran 1975 Satterfield 1991 Hydrocarbon Processing 1995		Pearce and Patterson suggests improved oxychlorination catalysts, and oxychlorination of ethane.	Process purpose is to utilize HCL produced in direct chlorination step. Dechlor process can be used to directly convert HCL to CL2 for recycle to direct dechlorination step. Satterfield describes other process configurations including those using CH4.
Ammonium nitrate				
Vinyl chloride	Hatch and Matar 1981 Lowenheim and Moran 1975 Hydrocarbon Processing 1995	Heat removal; competing reactions	Free radical chain mechanism. Presumably the conversion/pass is limited by heat release to control temperature	
Benzene	Lowenheim and Moran 1975, p. 126-33 Satterfield 1991 Hatch and Matar 1981		No clear strategy for improvement because multiple products are produced. Product removal in reactor may allow lower Rx temperatures to be used.	
	Lowenheim and Moran 1975 Satterfield 1991 Hatch and Matar 198, p. 148-49 Pearce and Patterson 1981		No clear strategy, competing hydrocracking reactions need to be minimized	
	Hatch and Matar 1981, p. 149 Lowenheim and Moran 1975, p. 129-30			
	Hatch and Matar 1981, p. 149		greater catalyst activity to achieve higher conversion without side Rx.. Removal of product	Minor process primarily used as a method of producing xylene
Ethylbenzene	Lowenheim and Moran 1975, p. 365 - 67 Hatch and Matar 1981, p. 137-8 Chenier 1986	xs benzene required for selective alkylation; high benzene separation and recycle load	Removal of ethylbenzene to prevent additional ethyl groups from adding to product. This won't improve overall yield as polyethylebenzenes are Rx in a separate step. Selective ethylene addition to prevent overalkylation and improve per pass yields	
	Lowenheim and Moran 1975, p. 367-370 Hatch and Matar p. 137-8		Removal of ethylbenzene to prevent additional ethyl groups from adding to product. This won't improve overall yield as polyethylebenzenes are Rx in a separate step.	
	Hatch and Matar 1981 Satterfield 1991		Removal of ethylbenzene to prevent additional ethyl groups from adding to product. This won't improve overall yield as polyethylebenzenes are Rx in a separate step.	Described under styrene synthesis in Satterfield 1991. Unocal has a zeolite cat. (H-Y type?) that operates at milder conditions in the liquid phase.
	Hatch and Matar 1981, p 138		NA	
MTBE	Satterfield, 1991, p. 260-1 Hatch and Matar 1983, p. 128-9 HP 1995, p. 110-12	Heat removal; mass transfer limitations	Heat removal and improved methanol macropore diffusion could improve conversion and selectivity. Improve catalyst activity to reduce Rx. temp.	Novel catalytic distillation technique has been used to improve conversion efficiency
Carbon dioxide				

Chemical	References	Process limitations	Strategies to overcome limitations	Other process notes
Styrene	Hatch and Matar 1981, p. 138-40 Satterfield 1991, p. 403-5 Lowenheim and Matar 1975, p. 779-82	Equilibrium-limited; heat addition; mass transfer limitations	Improve heat addition methods. Reduce diffusion limitation in catalyst. Separate hydrogen as it forms to break equilibrium	Noncatalytic (?) Epoxidation process (Chenier accts for 17% of production(1986) by oxidizing ethylbenzene and reacting with propylene to produce Propylene oxide and an alcohol dehydrated to styrene
	Chenier 1986 Hatch and Matar 1981 Satterfield 1991 Lowenheim and Moran 1975, p. 111 Pearce and Patterson 1981		improve selectivity of catalyst to coproducts	A titanium oxide catalyst may be required to dehydrogenate phenylmethylethanol to styrene at 180 - 280 C
Methanol	Hatch and Matar 1981 Satterfield 1991 Pearce and Patterson 1981 Hydrocarbon Processing 1995.	Equilibrium-limited; slow kinetics at low temperatures	remove CO, H ₂ as formed to improve conversion at lower temp Improve catalyst activity to lower temp. Separate methanol as it is formed to break equilibrium	
Formaldehyde	Hatch and Matar 1981 Pearce and Patterson 1981 Lowenheim and Moran 1975	Equilibrium-limited and unfavorable kinetics for undesired reactions.	catalyst improvement. Direct route from methane. Separate product as it is formed.	Satterfield notes that direct synthesis from methane has been tried but formaldehyde more reactive than methane (rapid quench or removal would make it more practical). Lowenheim and Moran describe methanol conversion process.
Xylene	Faith et. al 1975 Satterfield 1991 Hatch and Matar 1981		No clear strategy for improvement because multiple products are produced. Product removal in reactor may allow lower Rx temperatures to be used.	
	Hatch and Matar 1981, p. 149		greater catalyst activity to achieve higher conversion without side Rx.. Removal of product	Minor process primarily used as a method of producing benzene
	Faith et. al 1975 Satterfield 1991 Hatch and Matar 1981		No clear strategy for improvement because multiple products are produced. Product removal in reactor may allow lower Rx temperatures to be used.	
Toluene	Chenier 1986 Faith et. al 1975 Satterfield 1991 Hatch and Matar 1981		No clear strategy for improvement because multiple products are produced. Product removal in reactor may allow lower Rx temperatures to be used.	Very little difference between the toluene and benzene reforming routes except for the composition of the feed, and subsequent separations.
Hydrochloric acid				
p-Xylene	Petrochemical Handbook 1991	Equilibrium-limited	No clear strategy other than further improvement of catalyst selectivity. product removal may improve equilibrium (see xylene)	
	Hatch and Matar Satterfield 1991		Efficient removal of p-xylene as produced would improve yield.	References in Satter field on processes (p. 374)

Chemical	References	Process limitations	Strategies to overcome limitations	Other process notes
Terephthalic acid	Chenier 1986, p. 201-2 Hatch and Matar 1981, p. 160 Pearce and Patterson 1981 Lowenheim and Moran 1975, p. 807-9	Slow kinetics	Improved catalytic activity to avoid production of formylbenzoic acid due to underoxidation .	Hatch and Matar (p160) indicate a cobalt acetate catalyst promoted with NaBr or HBr, or by co-oxidizing acetaldehyde or MEK, this is a homogeneous catalyst(?)
	Hatch and Matar 1981, p 151-153		No apparent strategies. Probably similar to toluene disproportionation	
Ethylene oxide	Hatch and Matar 1981, p. 92-4 Lowenheim and Moran 1975 p. 408-10 Satterfield 1991	Heat removal; competing reactions which reduce selectivity; xs ethylene fed per pass = high separation and recycle load	Overreaction with O2 decreases selectivity with yield. Improve heat removal and in situ product removal.	Hatch and Matar give formulae and results for 3 catalysts. Alternative promoters listed by Lowenheim and Moran. Satterfield discusses possible role of Cl and alkali promoters. Leach 1983 gives good discussion of catalytic Rx.
Ethylene glycol	Hatch and Matar 1981 Lowenheim and Moran 1975 Pearce and Patterson 1981 Fahey 1987		No Specific strategies noted. Improved catalyst activity could reduce residence time	Hatch and Matar, Pearce and Patterson, and Fahey describe syngas routes, but none appear to be in practice. Ethylene Glycol produced intandem with ethylene oxide.
Ammonium sulfate				
Cumene	Chenier 1986, p. 178-9 Hatch and Matar 1981, p. 140-1 Lowenheim and Moran 1975	Competing reactions; xs benzene used to improve selectivity = large separation and recycle load	Improved selectivity of catalyst for cumene over other polyalkylated benzenes(overreaction occurs). Selective addition of propylene to control overreaction.	Assumes single pass which it is not.
Potash				
Phenol	Hatch and Matar 1981 Lowenheim and Moran 1975 Hydrocarbon Processing 1995 Pearce and Patterson 1981 Sittig 1968	Competing reactions	Improve selectivity of catalysts . removal of products to prevent overreaction	There are other processes of lesser importance including benzene sulfonation (5% of market), and benzene chlorination (3%)
Acetic acid	Hatch and Matar 1981, p. 101-2, Chenier 1986, p 155	Equilibrium-limited reaction; slow kinetics	No specific strategies identified.	
	Hatch and Matar 1981, p.66 Lowenheim and Moran 1975 Chenier 1986, p 156		No specific strategies noted	
	Hatch and Matar 1981, p. 55 Lowenheim and Moran 1975, p. 9-11 Chenier 1986. 155-6 Leach 1986, p. 275-95		increase reactivity of CO with methanol to achieve greater completion of reaction (produce better CO complex on catalyst at lower CO Partial pressures). Increase selectivity to acetic acid.	

Chemical	References	Process limitations	Strategies to overcome limitations	Other process notes
Butadiene	Pearce and Patterson, 1981, p. 285-6 Satterfield 1991, p. 290-1 Hatch and Matar 1981	Heat removal; catalyst deactivation; competing reactions which form CO ₂	The proc. is not equilibrium limited (because hydrogen prod. conv. to water) but rather limited by stoichiometry. Improved selectivity could produce modest energy improvements by reducing feedstock req. Improved heat removal would reduce stm/feed ratio.	Oxidative process accounts for 70% of Butene derived Butadiene. However, 95% of all butadiene is from steam cracking or imports. There are a number of catalyst systems and temperatures indicated in these references.
Carbon black	Hatch and Matar 1981, p. 88-9, Chenier 1986, p. 137 Satterfield 1991, p. 402-3 Lowenheim and Moran 1975, p. 165-8		Separate hydrogen as it forms to save valuable product rather than producing water. Control oxygen addition to keep catalyst coke-free while minimizing carbon oxide formation	Butylene Conv./pass = 25 - 30%. Butane conversion/pass = 11-11.5%.
Acrylonitrile	Hatch and Matar 1981, p. 106-7 Lowenheim and Moran 1975, p. 46-7 Chenier 1986, p. 136-7 Satterfield 1991, p. 273-77	Competing reactions to form acetonitrile and HCN; HCN recovered and acetonitrile incinerated???	Improve catalyst selectivity and stability	
Propylene oxide	Chenier 1986 Hatch and Matar 1981 Lowenheim and Moran 1975		No apparent strategy - noncatalytic process.	
Vinyl acetate	Chenier 1986 Hatch and Matar 1981, p. 109-11 Satterfield 1991, p. 285 Lowenheim and Moran 1975, p. 194-5 Pearce and Patterson 1981, pp. 149-50, 256-60	Competing reactions	Improve selectivity of catalyst for converting peroxide to product. Improve conversion of isobutane, ethylbenzene to hydroperoxide, using catalysts. Find direct oxidation catalyst	Hatch and Matar discuss other processes developed or considered. Satterfield indicates that Ethylbenzene and isobutane with isobutylene (and subsequently MTBE) produced with the latter.
Titanium dioxide	Hatch and Matar 1981, p. 102 Lowenheim and Moran 1975 Chenier 1986, p. 157-8 Satterfield 1991, p. 301-4	Mass transfer limitations; heat removal; lean-oxygen feed = high ethylene separation and recycle load	Improved selectivity by minimizing diffusion limitations	
Acetone	Hatch and Matar 1981, p. 140-2 Lowenheim and Moran 1975 Hydrocarbon Processing 1995 Pearce and Patterson 1981, p. 151-2	Competing reactions	Improve noncatalytic oxidation step. Improve selectivity of peroxide decomposition step	There are other processes of lesser importance including benzene sulfonation (5% of market), and benzene chlorination (3%)
	Hatch and Matar 1981 Lowenheim and Moran 1975 Chenier 1986		No apparent specific strategy.	There are other processes including as a coproduct in the noncatalytic production of hydrogen peroxide.
	Hatch and Matar 1981 Lowenheim and Moran 1975 Chenier 1986		No apparent specific strategy.	

Chemical	References	Process limitations	Strategies to overcome limitations	Other process notes
Cyclohexane	Hatch and Matar 1981 Lowenheim and Moran 1975 Chenier 1986 Satterfield 1991	Heat removal	improved heat removal to reduce isomerization	
Aluminum sulfate				
Sodium silicate				
Adipic acid	Hatch and Matar 1981, p. 146 Lowenheim and Moran 1975, p. 50-54 Pearce and Patterson 1981, p. 146	Competing reactions; heat removal	Improve selectivity of catalyst to produce hexanol/ hexanone intermediate or remove intermediate as formed. Improve selectivity of cat. for oxidation of intermediates.	preferred route
Calcium chloride	Hatch and Matar 1981		Better catalyst specificity	
Caprolactam	Lowenheim and Moran 1975, p. 201-3 Chenier 1986	Competing reactions	Improve selectivity. Selectivity may be due to over reaction or competing reactions.	Cyclohexanone can be made from cyclohexanol by dehydration over a zinc cat. (using the cyclohexanol/cyclohexanone intermediate from adipic acid route. Made from phenol by hydrogenation over Pd on carbon cat. there are other processes not used in US.
Sodium sulfate				
Isobutylene	HP 1995	kinetics to competing rxns, cat. deactivation; heat addition		
	Chenier 1986, p 175 Hatch and Matar 1981 p 111			

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