Green Engineering, Process Safety and Inherent Safety: A New Paradigm

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Presentation Outline

- Introduction to Green Engineering (GE) and Inherent Safety (IS)
  - GE definition, concepts, principles, and tools
  - IS concepts and tools
  - Similarities and differences between GE and IS

- Environmentally-Conscious Process Design Methodology
  - A hierarchical approach with three “tiers” of impact assessment
  - A case study for maleic anhydride (MA) process design
  - Early design methods and software tools
  - Flowsheet synthesis, assessment, and software tools
  - Flowsheet optimization - comparison of process improvement
  - Summary of environmentally-conscious design methods

What is Green Engineering?

Design, commercialization and use of processes and products that are *feasible* and *economical* while minimizing:

- \+ Risk to human health and the environment
- \+ Generation of pollution at the source

US EPA, OPPT, Chemical Engineering Branch, Green Engineering Program

Why Chemical Processes (USA)?

- Positives
  - 1 million jobs
  - $477.8 billion to the US economy
  - 5% of US GDP
  - + trade balance (in the recent past)
  - 57% reduction in toxic releases (`88-`00)

- *Chemical and Engineering News*, Vol. 80, No. 25, pp. 42-82, June 24, 2002
- US EPA, Toxics Release Inventory (TRI) Public Data Release, 2000

Why Chemical Processes (USA)?

- Environmental Challenges
  - Manufacturing industries in the US (SIC codes 20-39) *1/3* of all TRI releases
  - Chemical/Petroleum industries about *10%* of all TRI releases
  - Increase of *148%* of TRI wastes managed on-site (`91-`00)
  - Chemical products harm the environment during their *use*
  - Energy Utilization – ~15% of US consumption

- US EPA, Toxics Release Inventory (TRI) Public Data Release, 2000
- US DOE, Annual Energy Review, 1997.

Energy Use: U.S. Industry

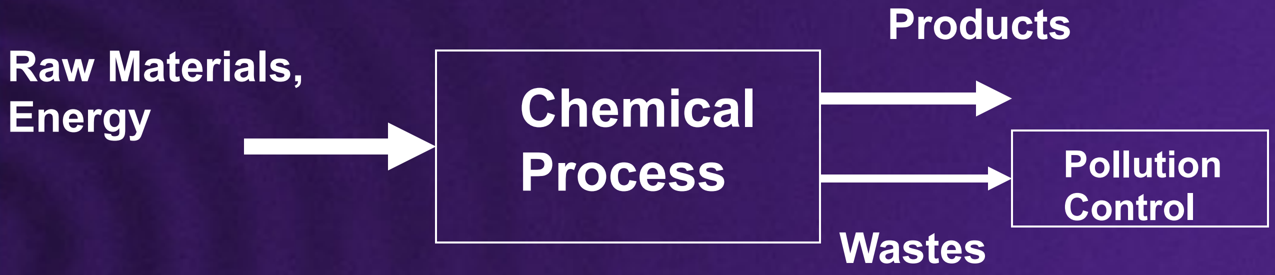
SIC Code	10^{15} BTU/yr
29 Petroleum/Coal Products	***6.34***
28 Chemicals / Allied Products	***5.33***
26 Paper / Allied Products	2.67
33 Primary Metals Industries	2.46
20 Food / Kindred Products	1.19
32 Stone,Clay and Glass	0.94
24 Lumber / Wood Products	0.49

Numbers represent roughly the % of US annual energy consumption

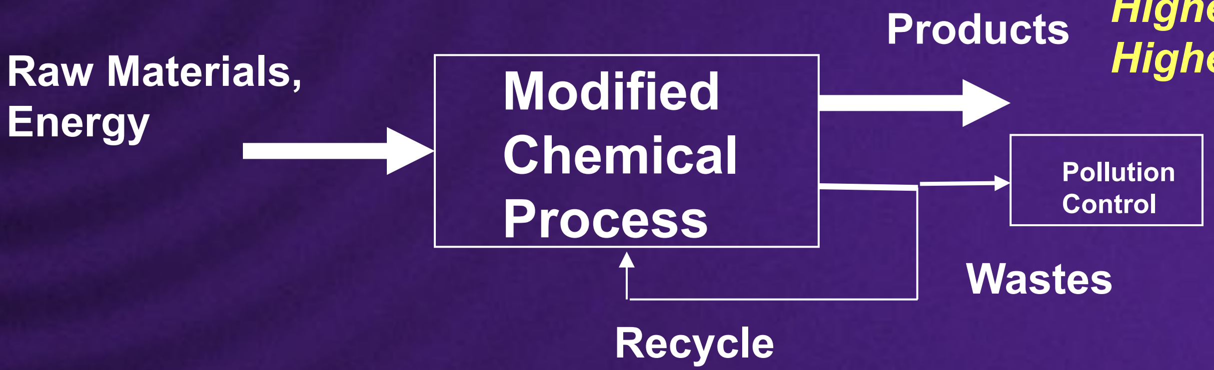
Annual Energy Review 1997, U.S. DOE, Energy Information Administration, Washington, DC, DOE/EIA-0384(97)

Pollution Prevention (P2) vs. Pollution Control (PC)

Traditional Process



Greener Process



Higher income, Higher operating costs

Lower PC costs

Examples of Green Engineering

- Chemical reactions using environmentally-benign solvents
- Improved catalysts
  - that increase selectivity and reduce wastes
  - that improve product quality and reduce environmental impacts
  - that process wastes into valuable products
- Separations using supercritical CO_2 rather than R-Cl solvents
- Separative reactors that boost yield and selectivity
- Fuel cells in transportation and electricity generation
- CO_2 sequestration
- New designs that integrate mass and energy more efficiently
- Process modifications that reduce emissions
- Environmentally-conscious design methods and software tools.

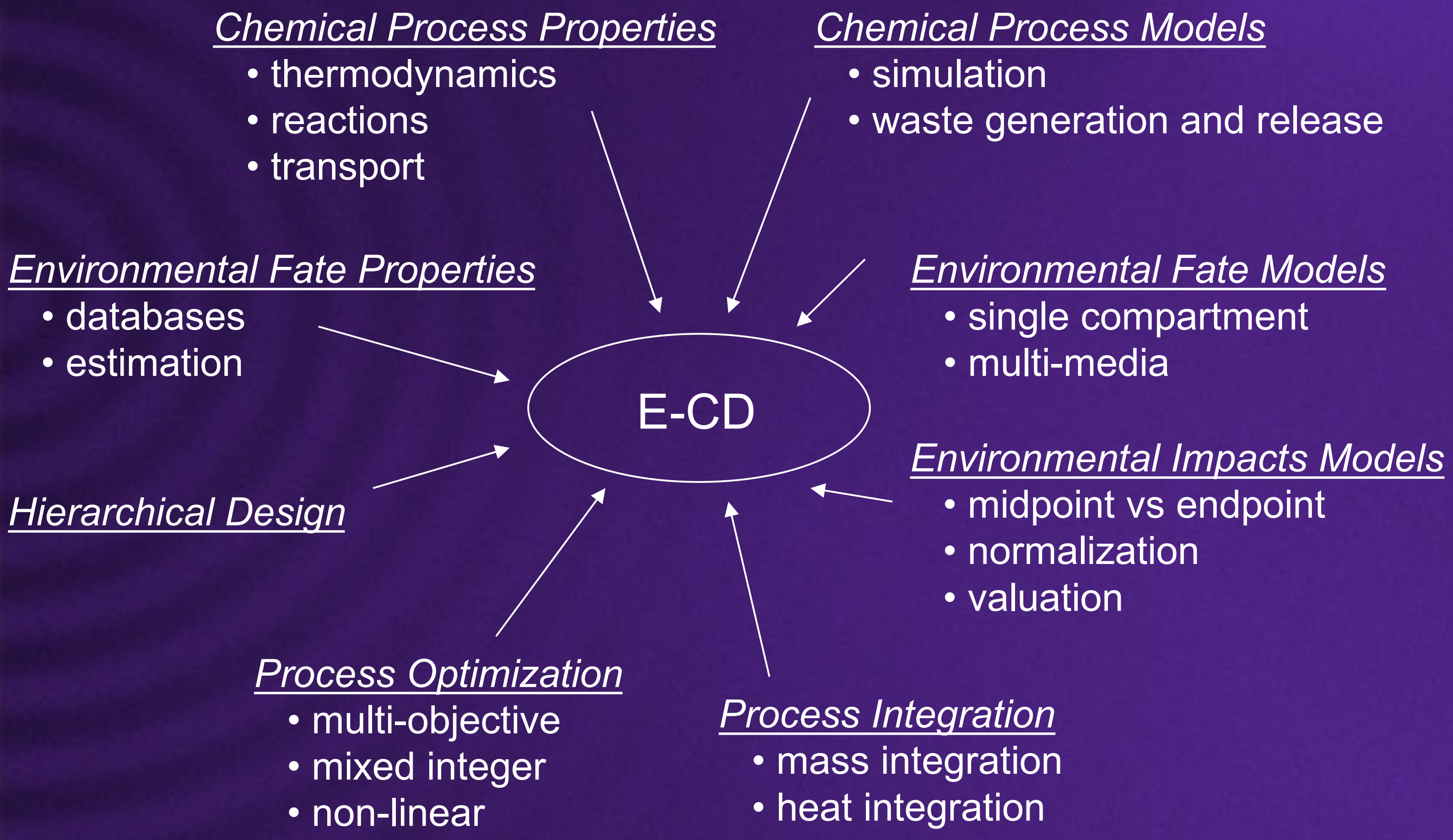
Environmentally-Conscious Design

- Methods and tools to evaluate environmental consequences of chemical processes and products are needed.
  - quantify multiple environmental impacts,
  - guide process and product design activities
  - improve environmental performance of chemical processes and products

- Environmental impacts
  - energy consumption
  - impacts to air, water
  - human health impacts
  - raw materials consumption
  - solid wastes
  - toxic effects to ecosystems

- Economic Performance
  - costs, profitability

Tools of Environmentally-Conscious Chemical Process Design and Analysis



Chemical Process Properties
- thermodynamics
- reactions
- transport

Chemical Process Models
- simulation
- waste generation and release

Environmental Fate Properties
- databases
- estimation

Environmental Fate Models
- single compartment
- multi-media

E-CD

Environmental Impacts Models
- midpoint vs endpoint
- normalization
- valuation

Hierarchical Design

Process Optimization
- multi-objective
- mixed integer
- non-linear

Process Integration
- mass integration
- heat integration

Principles of Green Engineering

The Sandestin Declaration on
Green Engineering Principles

Green Engineering transforms existing engineering disciplines and practices to those that lead to sustainability. Green Engineering incorporates development and implementation of products, processes, and systems that meet technical and cost objectives while protecting human health and welfare and elevates the protection of the biosphere as a criterion in engineering solutions.

Green Engineering: Defining the Principles, Engineering Conferences International, Sandestin, FL, USA, May 17-22, 2003.

Principles of Green Engineering

The Sandestin GE Principles

1. Engineer processes and products holistically, use systems analysis, and integrate environmental impact assessment tools.
2. Conserve and improve natural ecosystems while protecting human health and well-being
3. Use life-cycle thinking in all engineering activities
4. Ensure that all material and energy inputs and outputs are as inherently safe and benign as possible
5. Minimize depletion of natural resources
6. Strive to prevent waste
7. Develop and apply engineering solutions, while being cognizant of local geography, aspirations, and cultures
8. Create engineering solutions beyond current or dominant technologies; improve, innovate and invent (technologies) to achieve sustainability
9. Actively engage communities and stakeholders in development of engineering solutions

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Definition of Inherent Safety (IS)

A chemical manufacturing process is described as inherently safer if it reduces or eliminates hazards associated with materials used and operations, and this reduction or elimination is a permanent and inseparable part of the process technology. (Kletz, 1991; Hendershot, 1997a, b)

IS Concepts

- **Intensification** - using less of a hazardous material

  Example: improved catalysts can reduce the size of equipment and minimize consequences of accidents.

- **Attenuation** - using a hazardous material in a less hazardous form. Example: larger size of particle for flammable dust or a diluted form of hazardous material like aqueous acid rather than anhydrous acid.

- **Substitution** - using a safer material or production of a safer product. Example: substituting water for a flammable solvent in latex paints compared to oil base paints.

IS Concepts (cont.)

- **limitation -** minimizing the effect of an incident. Example: smaller diameter of pipe for transport of toxic gases and liquids will minimize the dispersion of the material when an accident does occur
- **Simplification -** reducing the opportunities for error and malfunction. Example: easier-to-understand instructions to operators.

Comparison between IS and (GE)

Strategy/Tenet (Based on IS)	Example Concepts	Inherent Safety (IS)	Green Engineering (GE)
Substitution	Reaction chemistry, Feedstocks, Catalysts, Solvents, Fuel selection	√√√√	√√√√
Minimization	Process Intensification, Recycle, Inventory reduction, Energy efficiency, Plant location	√√√	√√√√
Simplification	Number of unit operations, DCS configuration, Raw material quality, Equipment design	√√√√	√√√√
Moderation (1) [Basic Process]	Conversion conditions, Storage conditions, Dilution, Equipment overdesign	√√√√	√√√
Moderation (2) [Overall Plant]	Offsite reuse, Advanced waste treatment, Plant location, Beneficial co-disposal	√√√	√√√

√√√√ = Primary tenet/concepts √√√ = Strongly related tenet/concepts
√√ = Some aspects addressed √ = Little relationship

Similarities between (GE) and (IS)

- Benign and less hazardous materials.
- Both focus on process changes.
- Improving either one often results in improving the other.
- Both use a life-cycle approach.
- Both are best considered in the initial stages of the design.

Differences between GE & IS

- Focus on a different parts of the product life cycle.
- Focus on different aspect of EHS (environmental, health and safety) field and may conflict in application.
- Environmental impacts are more numerous than safety impacts.

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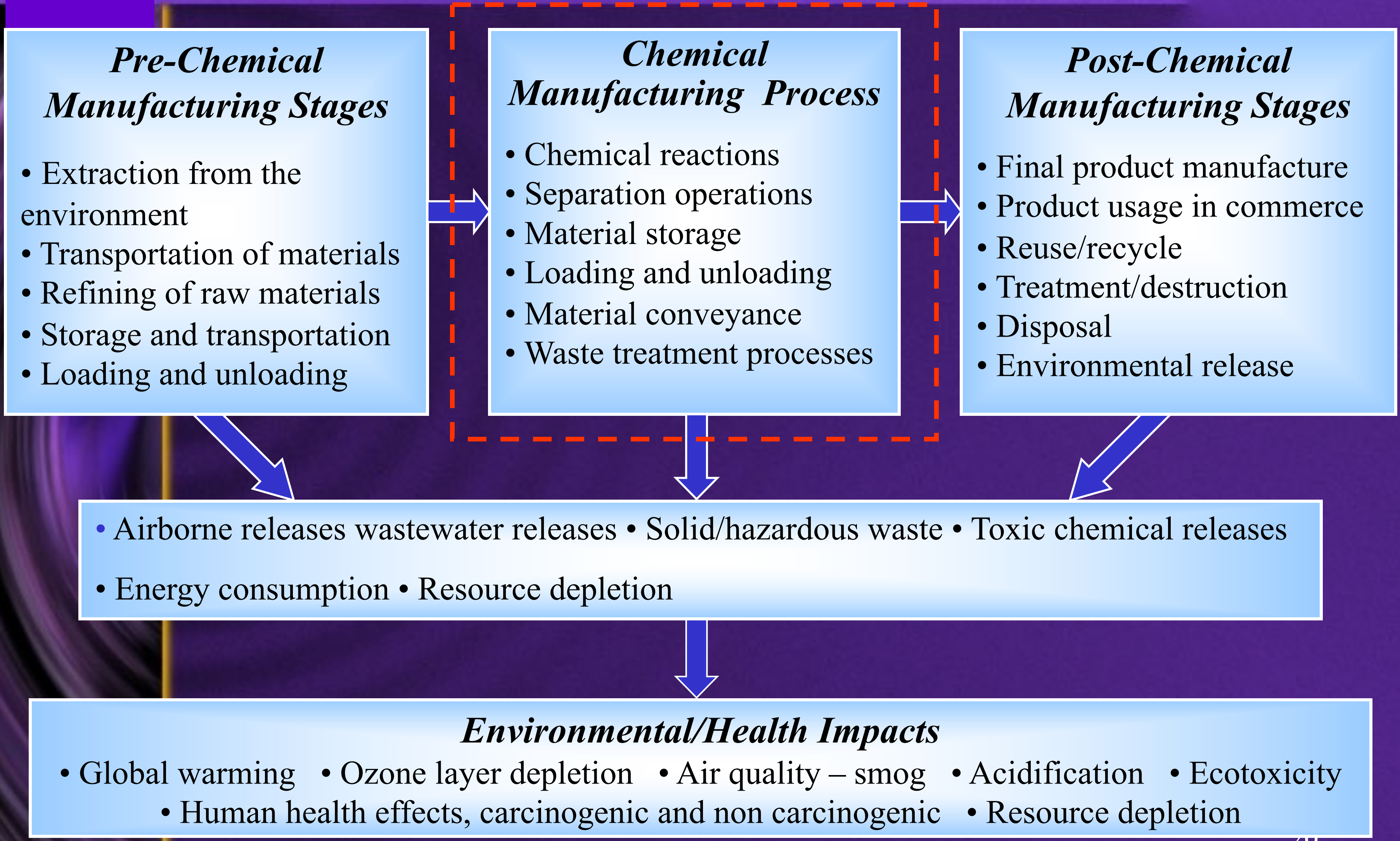
  - Summary of environmentally-conscious design (ECD) methods

Scope of environmental impacts



Pre-Chemical Manufacturing Stages

- Extraction from the environment
- Transportation of materials
- Refining of raw materials
- Storage and transportation
- Loading and unloading

Chemical Manufacturing Process

- Chemical reactions
- Separation operations
- Material storage
- Loading and unloading
- Material conveyance
- Waste treatment processes

Post-Chemical Manufacturing Stages

- Final product manufacture
- Product usage in commerce
- Reuse/recycle
- Treatment/destruction
- Disposal
- Environmental release

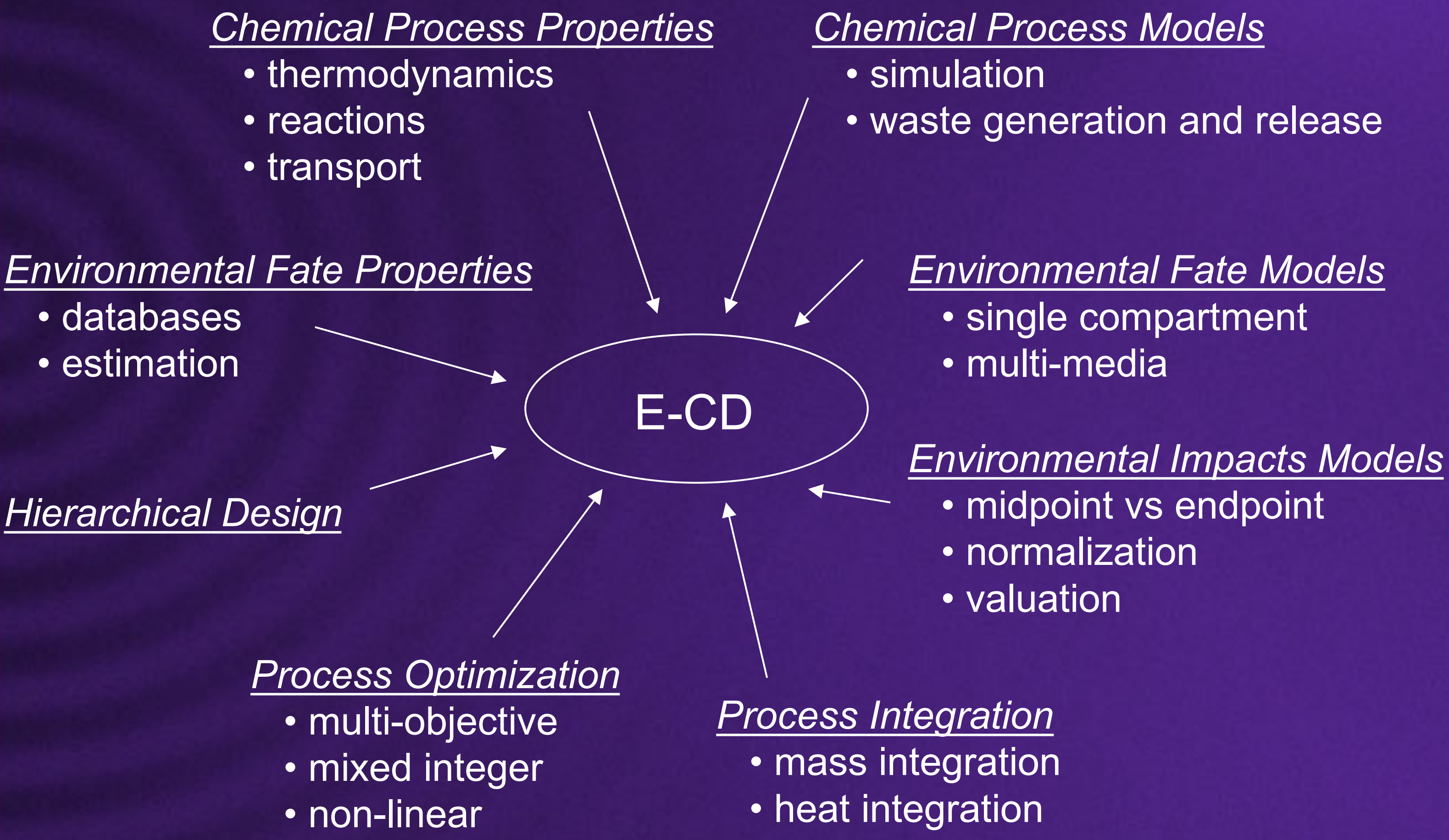
• Airborne releases wastewater releases • Solid/hazardous waste • Toxic chemical releases

• Energy consumption • Resource depletion

Environmental/Health Impacts

• Global warming • Ozone layer depletion • Air quality – smog • Acidification • Ecotoxicity
• Human health effects, carcinogenic and non carcinogenic • Resource depletion

Tools of Environmentally-Conscious Chemical Process Design and Analysis



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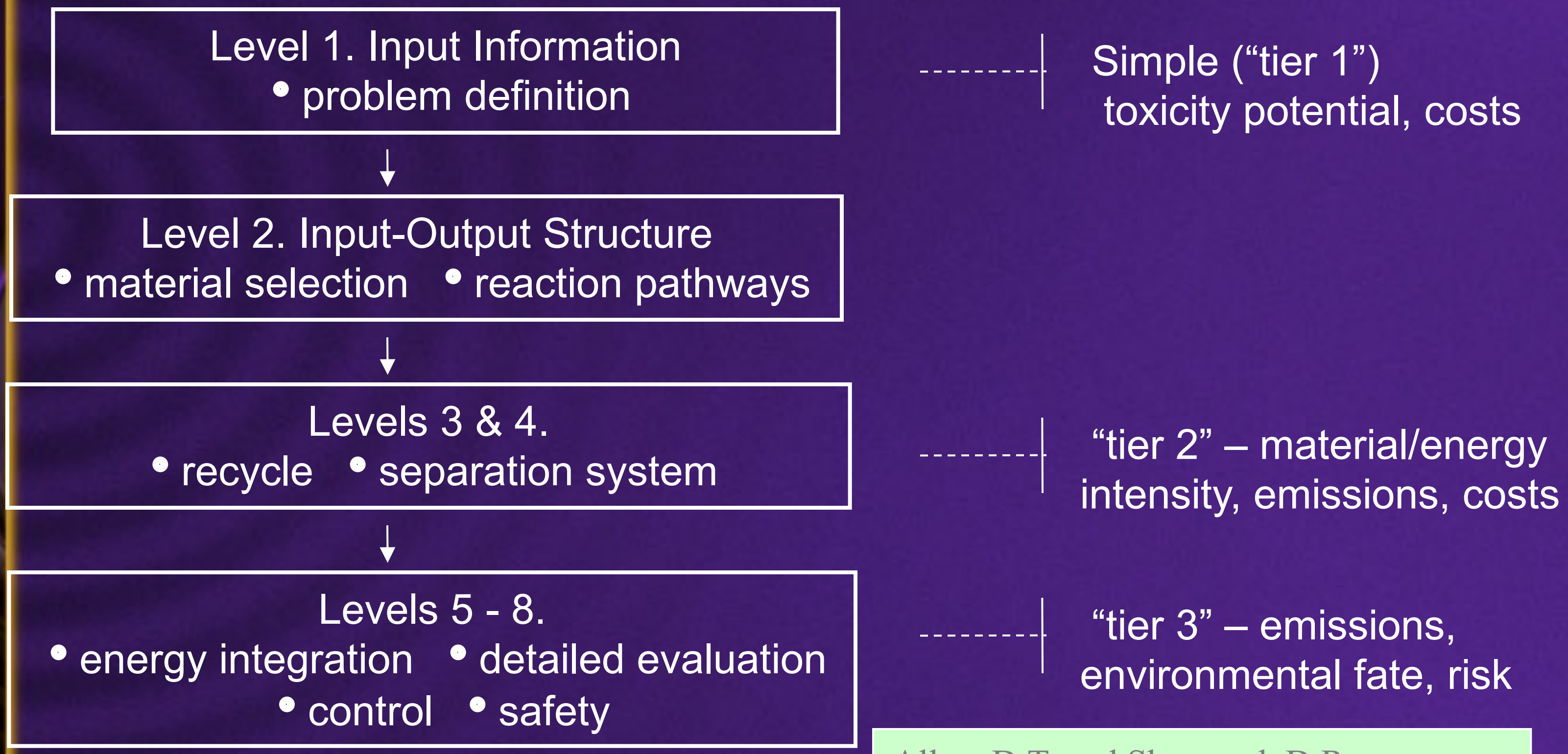
Hierarchical Approach to E-CD



Process Design Stages

Environmental Assessments

Level 1. Input Information
- problem definition

Simple ("tier 1")
toxicity potential, costs

Level 2. Input-Output Structure
- material selection
- reaction pathways

Levels 3 & 4.
- recycle
- separation system

"tier 2" – material/energy intensity, emissions, costs

Levels 5 - 8.
- energy integration
- detailed evaluation
- control
- safety

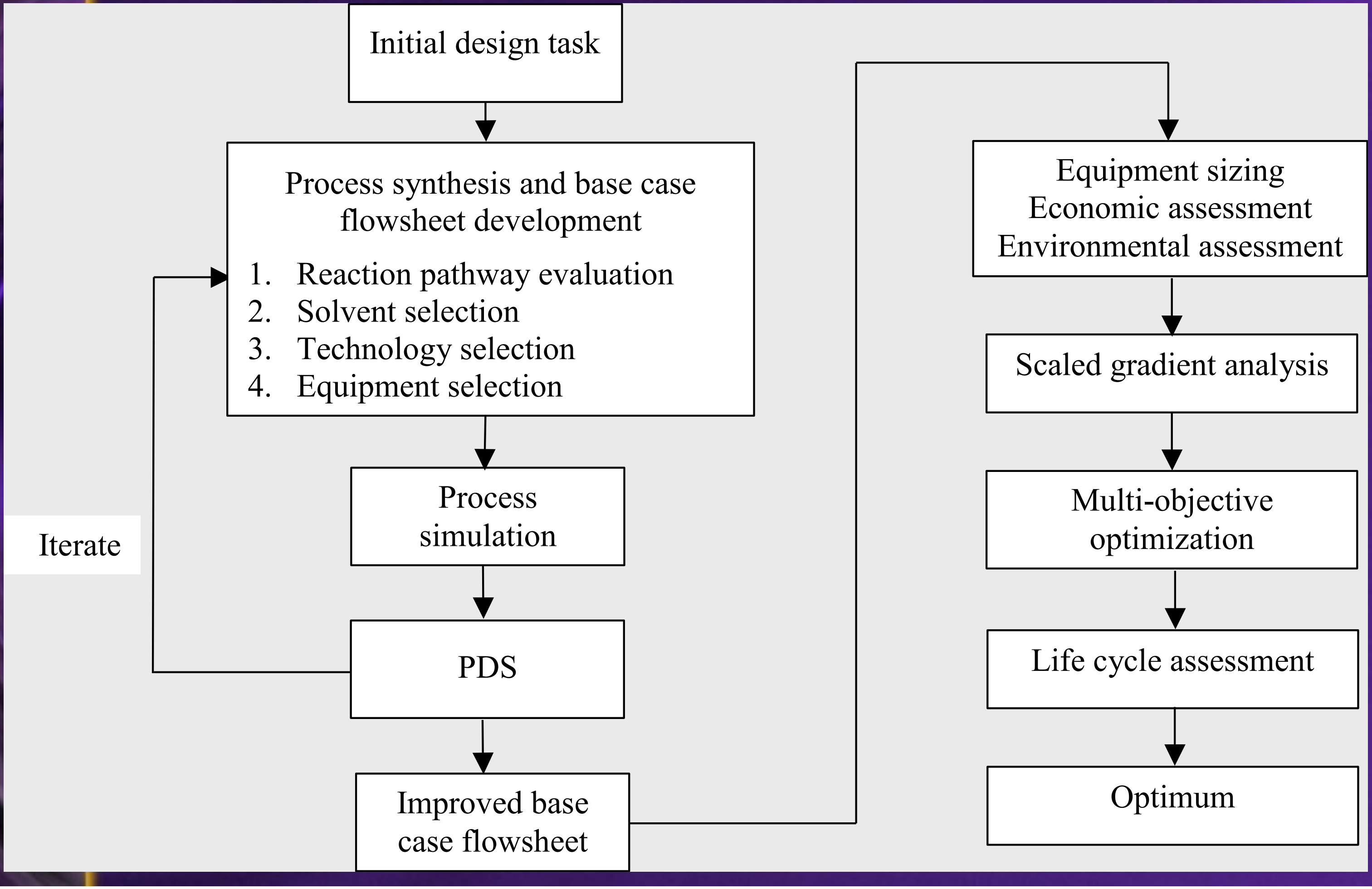
"tier 3" – emissions, environmental fate, risk

Douglas, J.M., *Ind. Eng. Chem. Res.*, Vol. 41, No. 25, pp. 2522, 1992

Allen, D.T. and Shonnard, D.R. *Green Engineering : Environmentally Conscious Design of Chemical Processes*, Prentice Hall, pg. 552, 2002.

Early vs Detailed Design Tasks

Chen, H., Rogers, T.N., Barna, B.A., Shonnard, D.R.,, *Environmental Progress*, in press April, 2003.



Initial design task

Process synthesis and base case flowsheet development

1. Reaction pathway evaluation
2. Solvent selection
3. Technology selection
4. Equipment selection

Process simulation

PDS

Iterate

Improved base case flowsheet

Equipment sizing
Economic assessment
Environmental assessment

Scaled gradient analysis

Multi-objective optimization

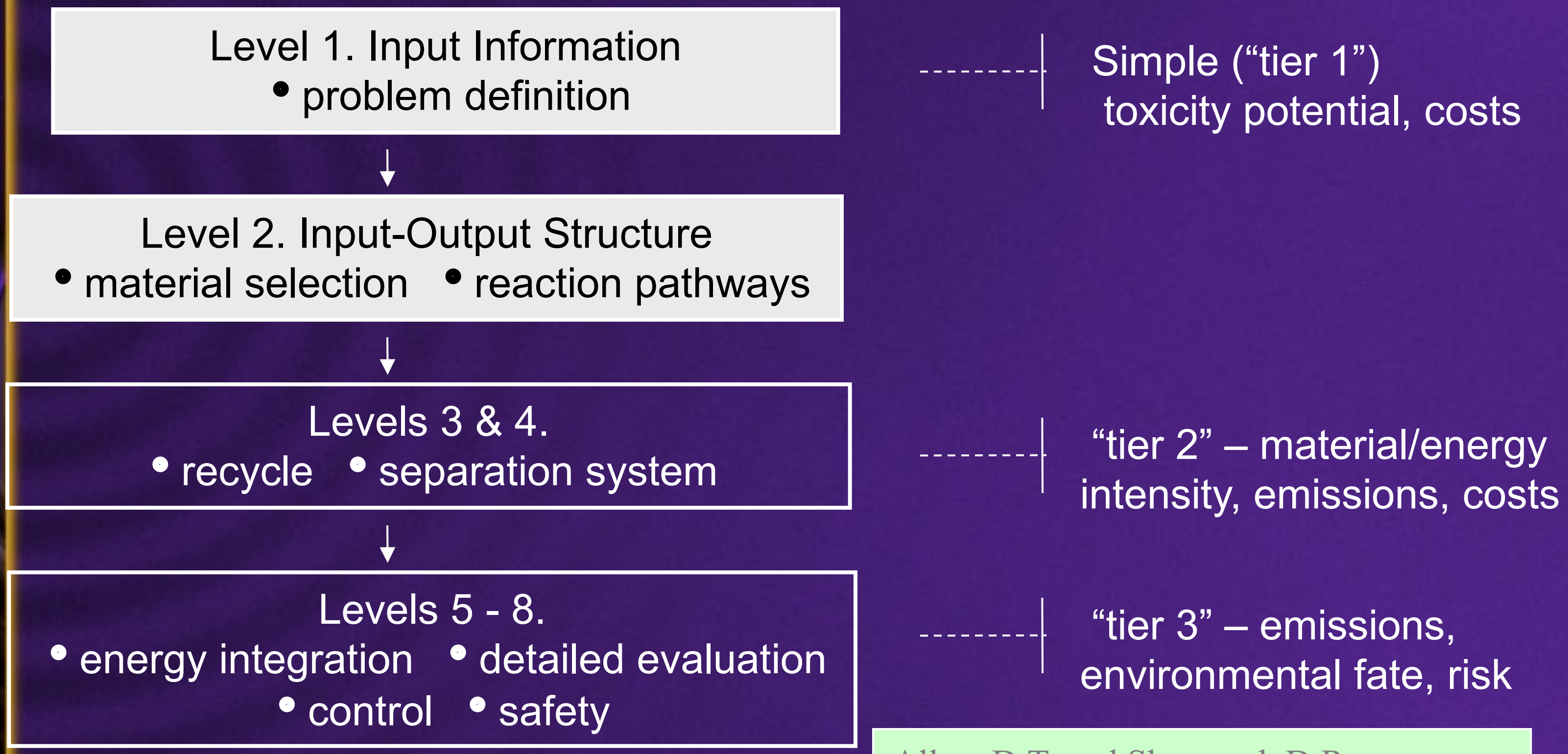
Life cycle assessment

Optimum

Early Design

Detailed Design

Hierarchical Approach to E-CD



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Case Study: Maleic Anhydride (MA) Production

Level 1. Input / Output Information

Benzene Process

V_2O_5-MoO_3

$$2C_6H_6 + 9O_2 \rightarrow 2C_4H_2O_3 + 4CO_2 + 4H_2O$$
$$2C_6H_6 + 9O_2 \rightarrow 12CO + 6H_2O$$
$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$$
$$C_4H_2O_3 + O_2 \rightarrow 4CO + H_2O$$
$$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O$$

Benzene conversion, 95%
MA Yield, 70%
Air/Benzene, ~ 66 (moles)
Temperature, 375°C
Pressure, 150 kPa

n-Butane Process

VPO

$$2C_4H_{10} + 7O_2 \rightarrow 2C_4H_2O_3 + 8H_2O$$
$$2C_4H_{10} + 9O_2 \rightarrow 8CO + 10H_2O$$
$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$$
$$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O$$
$$C_4H_2O_3 + O_2 \rightarrow 4CO + H_2O$$

n-butane conversion, 85%
MA Yield, 60%
Air/n-butane, ~ 62 (moles)
Temperature, 400°C
Pressure, 150 kPa

MA Production: Early Design Costs

Level 1. Input / Output Information

"Tier 1" Economic analysis (raw materials costs only)

Benzene Process

(1 mole/0.70 mole) × (78 g/mole) × (0.00028 $/g) = 0.0312 $/mole of MA

MA Yield | Bz MW | Benzene cost

N-butane process has lower cost

n-Butane Process

(1mole/0.60 mole) × (58 g/mole) × (0.00021 $/g) = 0.0203 $/mole of MA

MA Yield | nC4 MW | nC4 cost

Assumption: raw material costs dominate total cost of the process

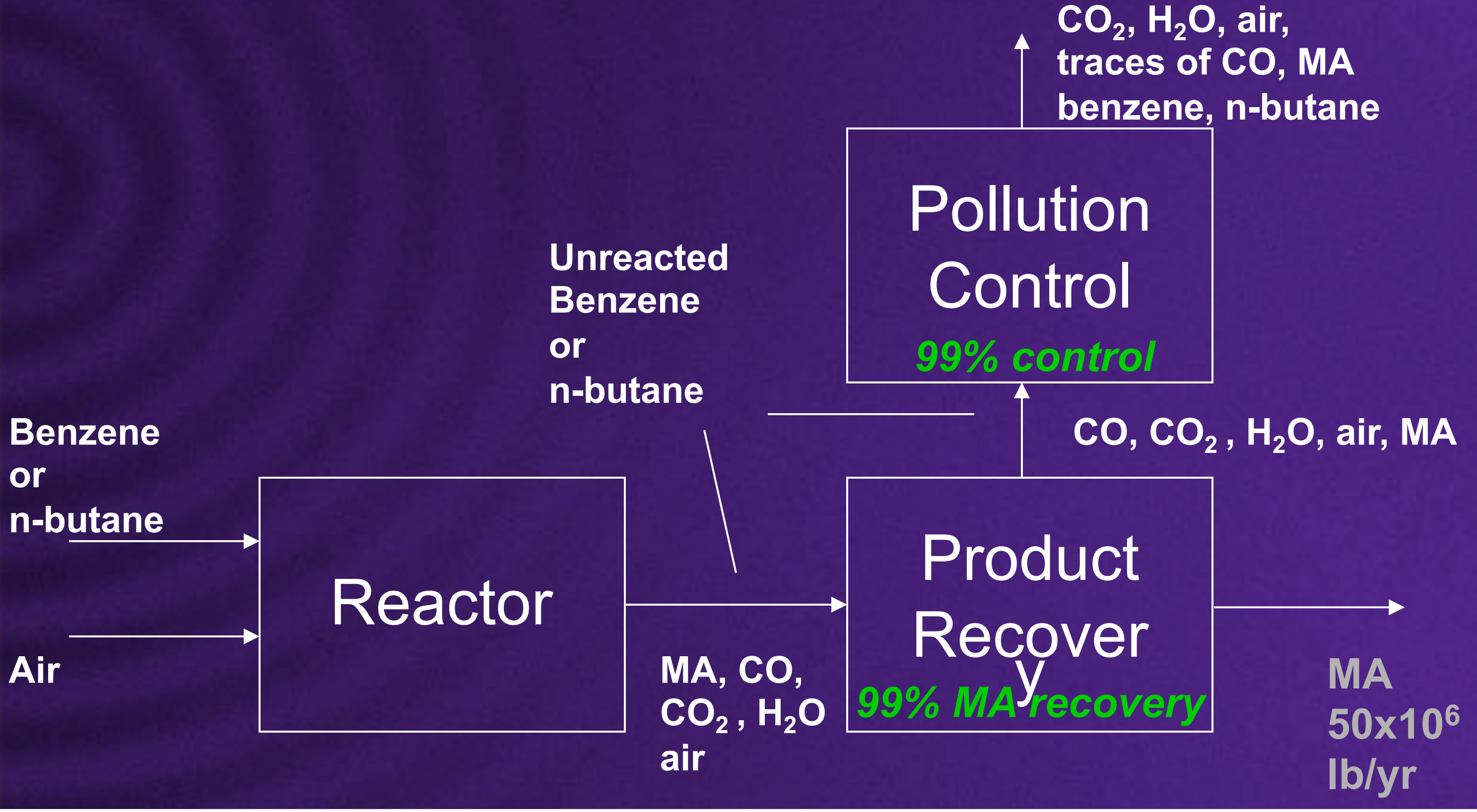
MA Production: Environmental Impacts

Level 1. Input / Output Information
“Tier 1” Environmental Impact Analysis

- Based on Products and Byproducts from the Reactor
- Alternative “tier 1” assessment approaches
  - Toxicity and stoichiometry
  - Toxicity, other impact potentials, and stoichiometry
  - Toxicity, other impact potentials, stoichiometry, and environmental fate
  - **Toxicity, other impact potentials, stoichiometry, environmental fate, and pollution control**.

MA Production: IO Assumptions

Level 1. Input / Output Information
“Tier 1” Environmental Impact Analysis



CO_2, H_2O, air,
traces of CO, MA
benzene, n-butane

Pollution Control

99% control

Unreacted
Benzene
or
n-butane

CO, CO_2 , H_2O, air, MA

Benzene
or
n-butane

Air

Reactor

MA, CO,
CO_2 , H_2O
air

Product Recovery

99% MA recovery

MA
$50x10^6$
lb/yr

Emission Estimation

Level 1. Input / Output Information
"Tier 1" Environmental Impact Analysis

- Emissions to Air
  - Emission factors from US EPA
    - Reactors, separation devices
    - Air ClearingHouse for Inventories and Emission Factors
    - Air CHIEF http://www.epa.gov/ttn/chief/index.html
  - CO, CO_2 generation from the reactor
    - Benzene process
      - Benzene: 0.07 moles benzene / mole MA
      - CO + CO_2: 4.1 moles / mole MA
    - n-butane process
      - n-butane: 0.25 moles benzene / mole MA
      - CO + CO_2: 1.7 moles / mole MA

Conversions, Yields

Environmental / Toxicity Properties

Level 1. Input / Output Information
"Tier 1" Environmental Impact Analysis

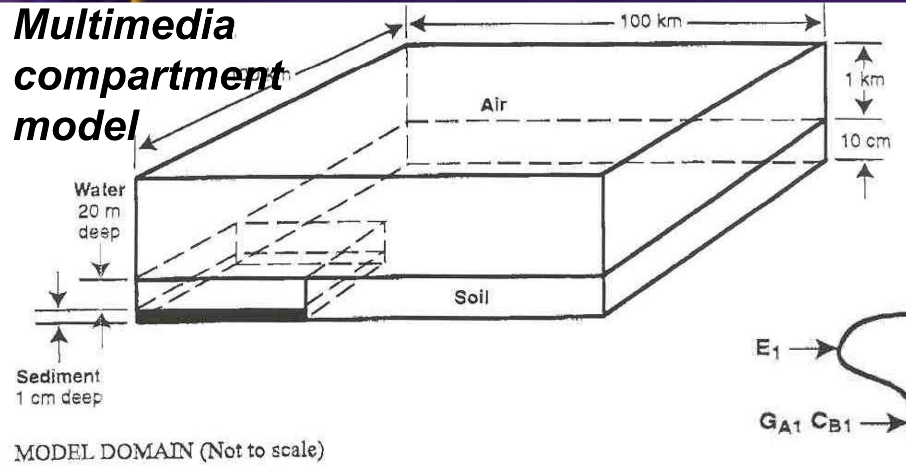
- Environmental/Toxicological Properties
  - Estimation Software
    - EPI (Estimation Program Interface) Suite
    - http://www.epa.gov/oppt/exposure/docs/episuite.htm
    - Henry's constant, partitioning, degradation, toxicity
  - Online Database
    - Environmental Fate Database
    - http://es.epa.gov/ssds.html

Compilation in: Appendix F.
Allen, D.T. and Shonnard, D.R., *Green Engineering : Environmentally- Conscious Design of Chemical Processes*, Prentice Hall, pg. 552, 2002

Environmental Fate Calculations

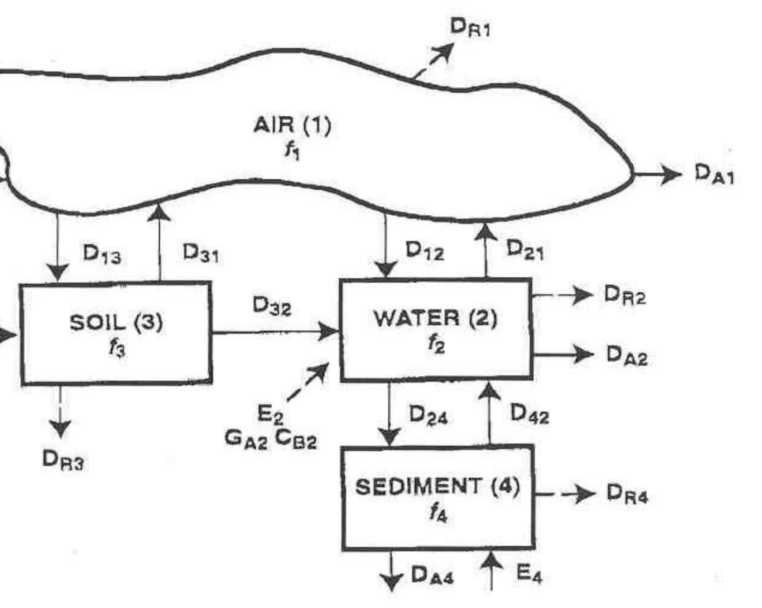
Level 1. Input / Output Information
"Tier 1" Environmental Impact Analysis

Multimedia compartment model



Processes modeled

- emission inputs, *E*
- advection in and out, D_A
- intercompartment mass transfer, $D_{i,j}$
- reaction loss, D_R



Model Domain Parameters

- surface area - 10^4 -10^5 km^2
- 90% land area, 10% water
- height of atmosphere - 1 km
- soil depth - 10 cm
- depth of sediment layer - 1 cm
- multiphase compartments

Mackay, D. 1991, "Multimedia Environmental Models", 1st edition,, Lewis Publishers, Chelsea, MI

Impact Indicator Calculation

Level 1. Input / Output Information
“Tier 1” Environmental Impact Analysis

Carcinogenic Risk Example (inhalation route)

$$\text{Relative Risk} = \frac{\left[\frac{(C_a \times CR \times EF \times ED)}{(BW \times AT)} \times SF\right]_i}{\left[\underbrace{\frac{(C_a \times CR \times EF \times ED)}{(BW \times AT)}} \times SF\right]_{Benchmark}}$$

$$= \frac{\left[C_a \times SF\right]_i}{\left[C_a \times SF\right]_{Benchmark}}$$

Exposure Factors

Multimedia compartment model concentration in air

Carcinogenic Slope Factor, SF (toxicological property)

Indicators for the Ambient Environment

Level 1. Input / Output Information
“Tier 1” Environmental Impact Analysis

The TRACI method and software contains a comprehensive listing of impact categories and indicators.

Relative Risk Index	Equation
Global Warming	$I^*_{GW,i} = GWP_i$
	$I^*_{GW,i} = N_C \frac{MW_{CO_2}}{MW_i}$
Ozone Depletion	$I^*_{OD,i} = ODP_i$
Smog Formation	$I^*_{SF,i} = \frac{MIR_i}{MIR_{ROG}}$
Acid Rain	$I^*_{AR,i} = \frac{ARP_i}{ARP_{SO_2}}$

GWP = global warming potential, $\boldsymbol{N_C}$ = number of carbons atoms, ***ODP*** = ozone depletion potental, ***MIR*** = maximum incremental reactivity, ***ARP*** = acid rain potential.

Compilation impact parameters in: Appendix D.
Allen, D.T. and Shonnard, D.R., *Green Engineering : Environmentally-Conscious Design of Chemical Processes*, Prentice Hall, pg. 552, 2002

Indicators of Toxicity

Level 1. Input / Output Information
“Tier 1” Environmental Impact Analysis

The TRACI method and software contains a comprehensive listing of impact categories and indicators.

Relative Risk Index	Equation
Human Toxicity Ingestion Route	$I^*_{ING} = \frac{C_{W,i}\ LD_{50,Toluene}}{C_{W,Toluene}\ LD_{50,i}}$
Human Toxicity Inhalation Route	$I^*_{INH} = \frac{C_{A,i}\ LC_{50,Toluene}}{C_{A,Toluene}\ LC_{50,i}}$
Human Carcinogenicity Ingestion Route	$I^*_{CING} = \frac{C_{W,i}\ HV_i}{C_{W,Benzene}\ HV_{Benzene}}$
Human Carcinogenicity Inhalation Route	$I^*_{CINH} = \frac{C_{A,i}\ HV_i}{C_{A,Benzene} HV_{Benzene}}$
Fish Toxicity	$I^*_{FT} = \frac{C_{W,i}\ LC_{50\ f,PCP}}{C_{W,PCP}\ LC_{50\ f,i}}$

LD$_{50}$ = lethal dose 50% mortality, **LC$_{50}$** = lethal concentration 50% mortality and **HV** = hazard value for carcinogenic health effects.

Indicators for MA Production

Level 1. Input / Output Information
"Tier 1" Environmental Impact Analysis

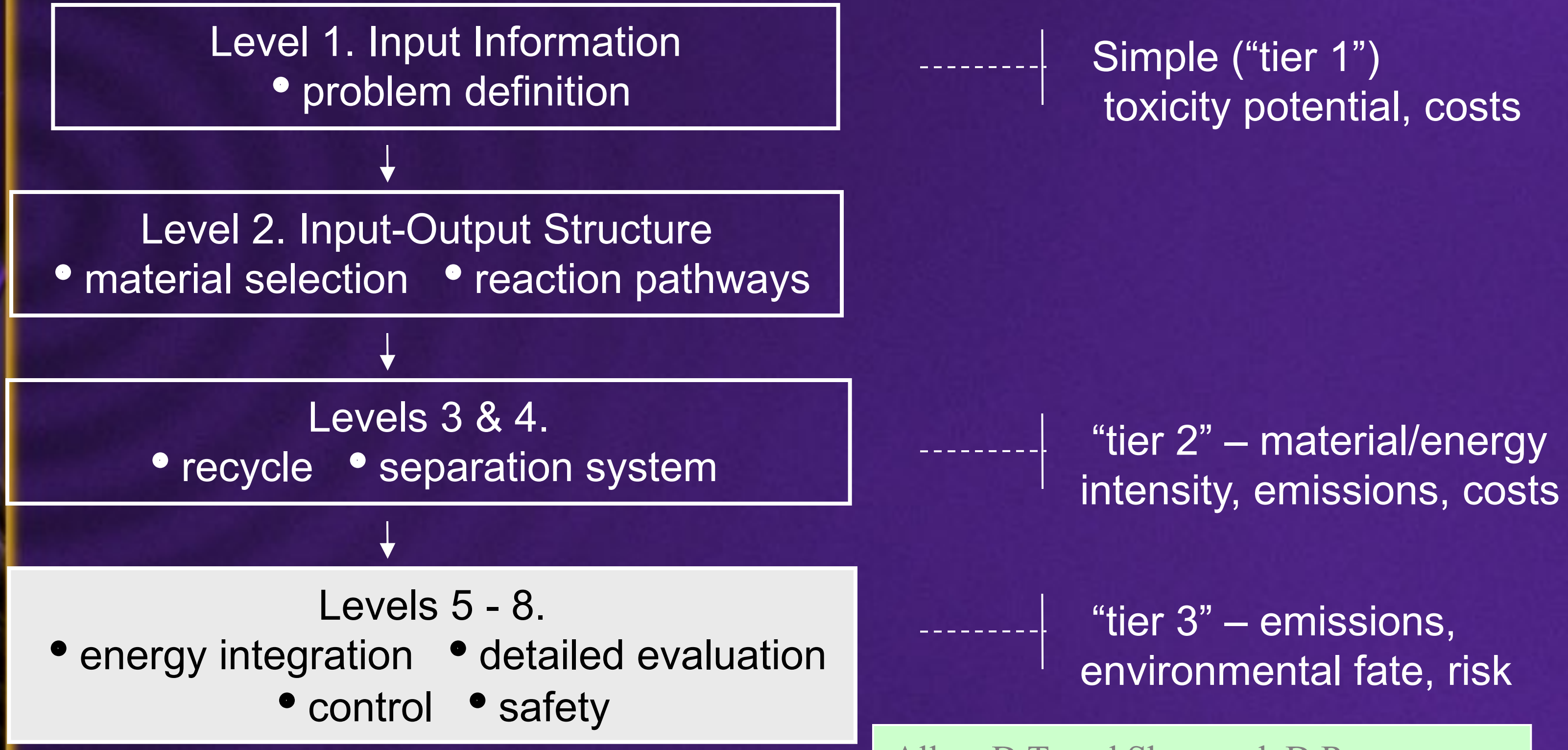
$$\text{Process Index } (I) = \sum_{i=1}^{N} (I_i^*) \times (m_i)$$

Chemical	Benzene	n-butane
I_{FT} **(kg/mole MA)**	$5.39\text{x}10^{-6}$	$2.19\text{x}10^{-6}$
I_{ING} "	$3.32\text{x}10^{-3}$	$3.11\text{x}10^{-3}$
I_{INH} "	$8.88\text{x}10^{-2}$	$3.93\text{x}10^{-2}$
I_{CING} "	$1.43\text{x}10^{-4}$	0.00
I_{CINH} "	$1.43\text{x}10^{-4}$	0.00
I_{OD} "	0.00	0.00
I_{GW} "	$2.01\text{x}10^{-1}$	$1.17\text{x}10^{-1}$
I_{SF} "	$3.04\text{x}10^{-5}$	$4.55\text{x}10^{-6}$
I_{AR} "	0.00	0.00

n-butane process has lower environmental impacts

Hierarchical Approach to E-CD

Process Design Stages | **Environmental Assessments**



Level 1. Input Information
- problem definition

↓

Level 2. Input-Output Structure
- material selection
- reaction pathways

↓

Levels 3 & 4.
- recycle
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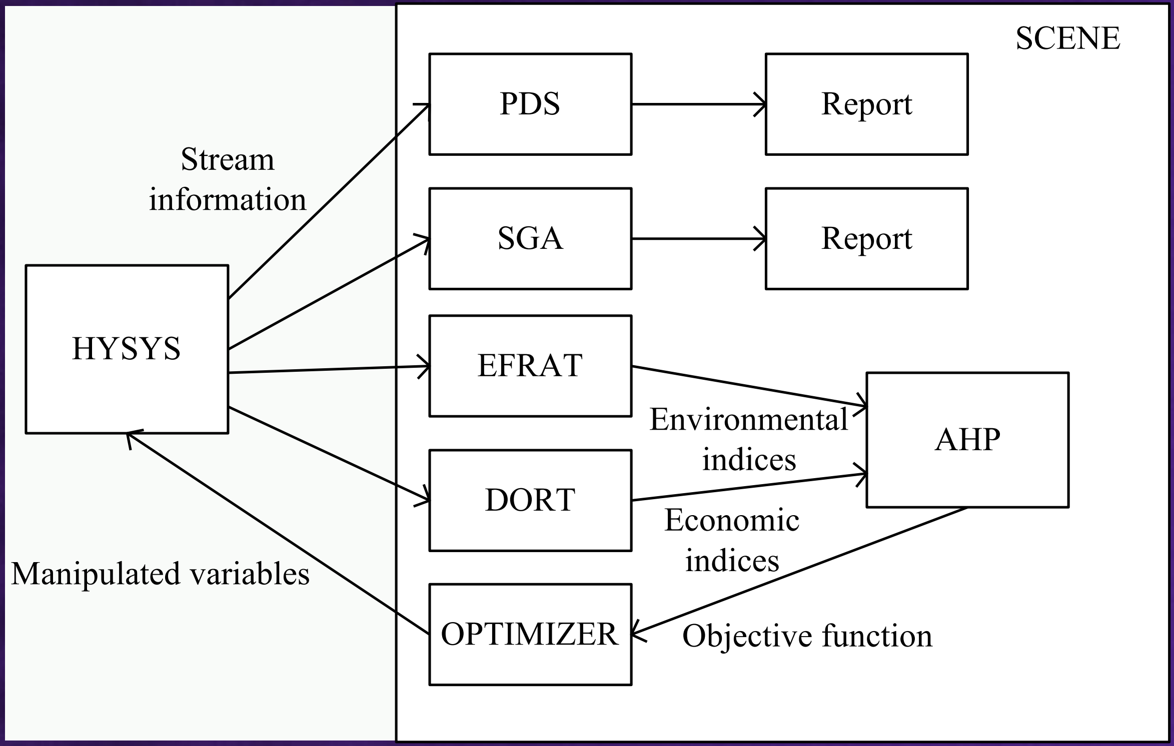
Case Study: MA Production

Level 3-8. Flowsheet Synthesis and Evaluation
“Tier 3” Environmental Impact Analysis

- Based on an initial process flowsheet created using “traditional“ economic-based design *heuristics*.

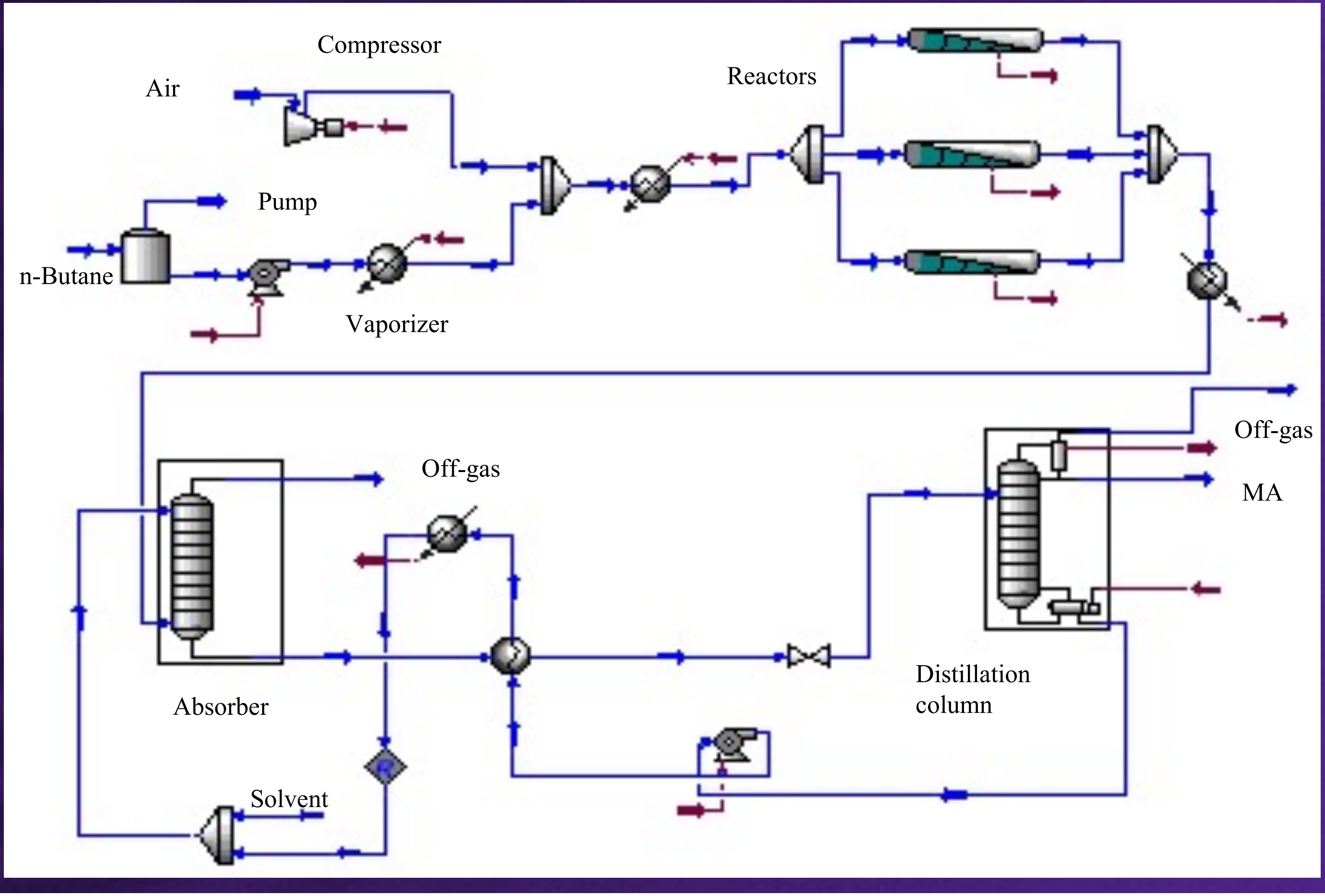
- “tier 3” assessment
  - Emissions estimation from units and fugitive sources
  - Environmental fate and transport calculation
  - Toxicity, other impact potentials, environmental fate and transport, and pollution control.

Integrated Process Simulation and Assessment Method and Software



HYSYS – a commercial chemical process simulator software, **EFRAT** – a software for calculating environmental impacts, **DORT** - a software to estimate equipment costs and operating costs, **AHP** (Analytic Hierarchy Process) – multi-objective decision analysis, **PDS** – Process Diagnostic Summary Tables, **SGA** – Scaled Gradient Analysis

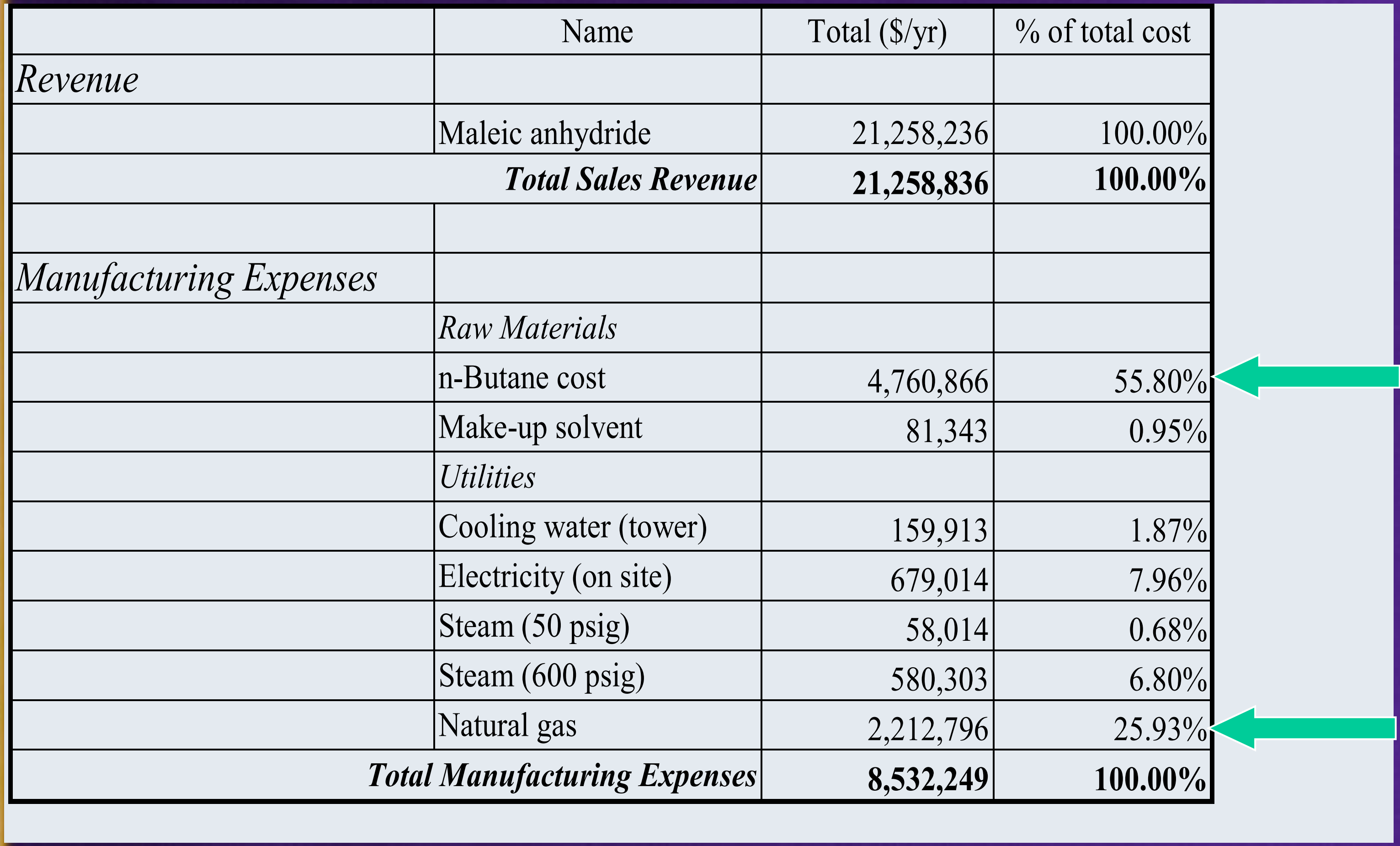
Initial Flowsheet for MA from n-C4



Process Diagnostic Summary Tables: Energy Input/Output for nC4 Process

Stream	Available temperature (In,Out)(?F)	Available Pressure (In,Out)(psia)	Energy flow (MM Btu/hr)	% of total energy
	Input			
Air	77	14.696	0.0000	0.00%
n-Butane	50	22.278	-0.0424	-0.11%
Make-up solvent	95	18.13	0.0004	0.00%
Solvent pump	472.87~472.96	1.2505~18.13	0.0107	0.03%
Air compressor	77~167.18	14.696~22.278	3.9588	9.92%
n-Butane vaporizer	50~50.004	22.278	1.0059	2.52%
Reactor feed heater	160.62~770	22.278	29.8800	74.90%
Reboiler	472.87	1.2505	5.0774	12.73%
Total			39.8908	100.00%
	Output			
Absorber off-gas	120.53	18.275	2.0033	1.80%
Distillation off-gas	95.043	0.3897	0.0002	0.00%
Crude MA	95.043	0.3897	0.0368	0.03%
Reactor 1	770		23.6340	21.29%
Reactor 2	770		23.6340	21.29%
Reactor 3	770		23.6340	21.29%
Reactor off-gas cooler	770~230	18.943	26.8940	24.23%
Solvent subcooler	234.95~95	18.13	7.1588	6.45%
Condenser	95.043	0.3897	4.0202	3.62%
Total			111.0153	100.00%

Process Diagnostic Summary Tables: Manufacturing Profit and Loss, nC4



	Name	Total ($/yr)	% of total cost
Revenue			
	Maleic anhydride	21,258,236	100.00%
Total Sales Revenue		**21,258,836**	**100.00%**
Manufacturing Expenses			
	Raw Materials		
	n-Butane cost	4,760,866	55.80%
	Make-up solvent	81,343	0.95%
	Utilities		
	Cooling water (tower)	159,913	1.87%
	Electricity (on site)	679,014	7.96%
	Steam (50 psig)	58,014	0.68%
	Steam (600 psig)	580,303	6.80%
	Natural gas	2,212,796	25.93%
Total Manufacturing Expenses		**8,532,249**	**100.00%**

Process Diagnostic Summary Tables: Environmental Impacts, nC4

Normalization

$$I_N^k = \frac{I_k}{\breve{U} I_k}$$

Process Index

National Index

Chemical	I_{FT}	I_{ING}	I_{INH}	I_{CING}	I_{CINH}	I_{OD}	I_{GW}	I_{SF}	I_{AR}
Sulfur dioxide	0.00E+00	0.00E+00	1.49E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.35E+02
TOC	1.36E-02	1.49E-02	6.62E+01	0.00E+00	0.00E+00	0.00E+00	4.11E+03	4.24E+02	0.00E+00
Carbon dioxide	4.36E+02	0.00E+00	8.91E+01	0.00E+00	0.00E+00	0.00E+00	6.09E+07	0.00E+00	0.00E+00
Carbon monoxide	1.90E-01	0.00E+00	1.65E+07	0.00E+00	0.00E+00	0.00E+00	2.33E+05	2.03E+03	0.00E+00
Dibutyl phthalate	7.70E+01	1.00E+02	3.01E+00	0.00E+00	0.00E+00	0.00E+00	2.56E+02	0.00E+00	0.00E+00
Maleic Anhydride	5.10E+02	7.27E+05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.49E+04	0.00E+00	0.00E+00
n-Butane	6.98E-02	0.00E+00	2.38E+05	0.00E+00	0.00E+00	0.00E+00	6.97E+04	0.00E+00	0.00E+00
Nitrogen dioxide	2.10E-01	0.00E+00	2.89E+03	0.00E+00	0.00E+00	0.00E+00	4.09E+06	0.00E+00	7.16E+04
Totals	1.02E+03	7.27E+05	1.67E+07	0.00E+00	0.00E+00	0.00E+00	6.54E+07	2.46E+03	7.17E+04
Contribution to I_{PC}	1.55%	0.34%	86.63%	0.00%	0.00%	0.00%	4.85%	0.14%	6.50%
I_{PC}	6.13E-04								

Process composite index

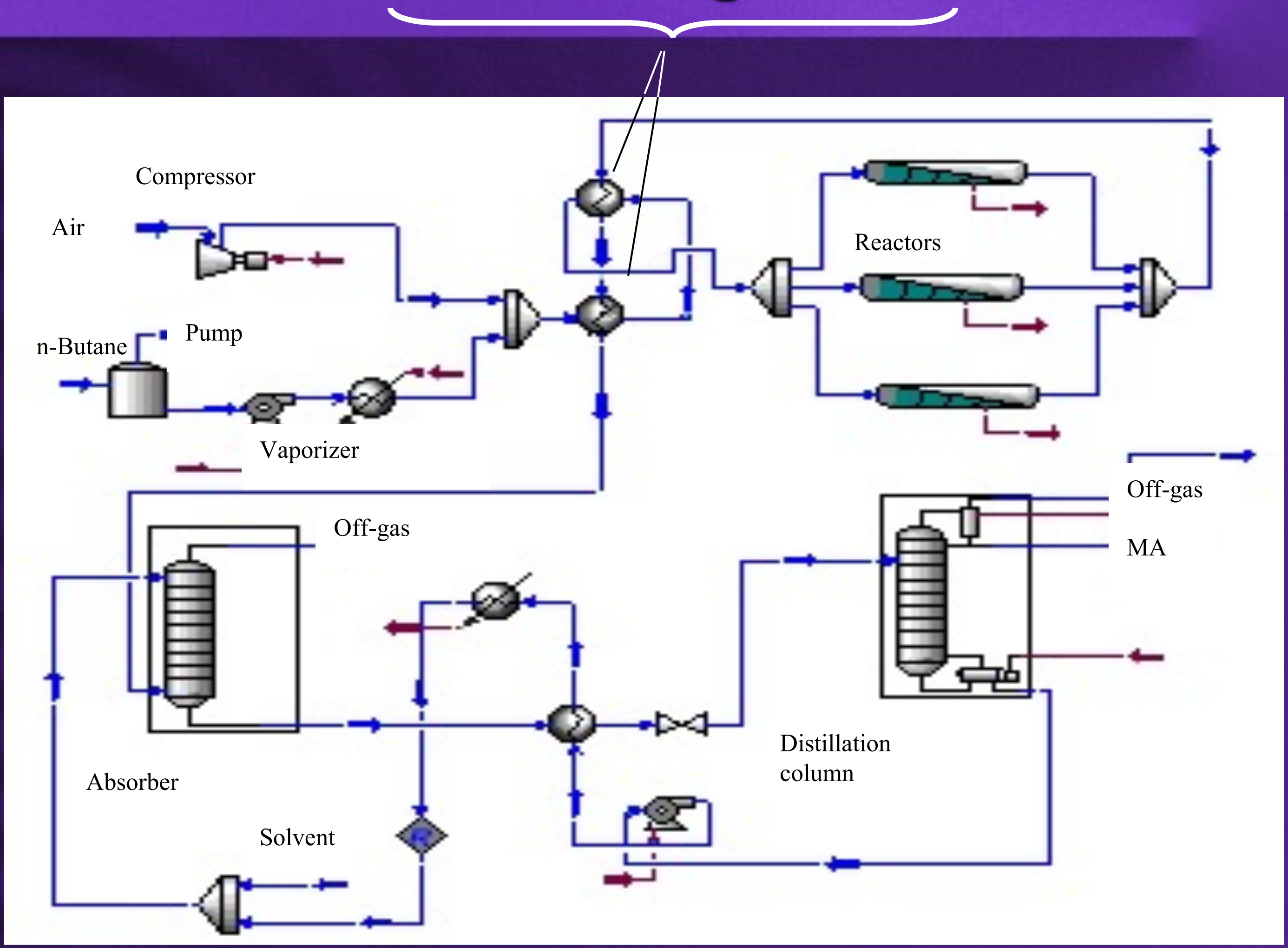
$$I_{PC} = \sum_k (I_N^k \times W_k)$$

Weighting Factors

global warming	*2.5*
ozone depletion	*100*
smog formation	*2.5*
acid rain	*10*
carcinogenic	*5*
noncarcinogenic	*5*
ecotoxicity	*10*

Source: Eco-Indicator 95 framework for life cycle assessment, Pre Consultants, http://www.pre.nl

Flowsheet for MA Production from n-C4: with Heat Integration.



Scaled Gradient Analysis

Flowsheet Optimization:
Scaled Gradient Analysis (SGA):

Rank Order Parameter, r_j
i = i-th unit operation
j = j-th design variable

Proximity Parameter, p_j
i = i-th unit operation
j = j-th design variable

$$r_j = \sum_i \left| \frac{\partial I_i}{\partial x_j} \right| \Delta x_j$$

$$p_j = \frac{\left| \left(\sum_i \partial I_i \Big/ \partial x_j \right) \Delta x_j \right|}{\sum_i \left| \partial I_i / \partial x_j \right| \Delta x_j}$$

Douglas, J. M., "Conceptual Design of Chemical Process," McGraw-Hill, New York (1988).

SGA: variable changes and scale factors

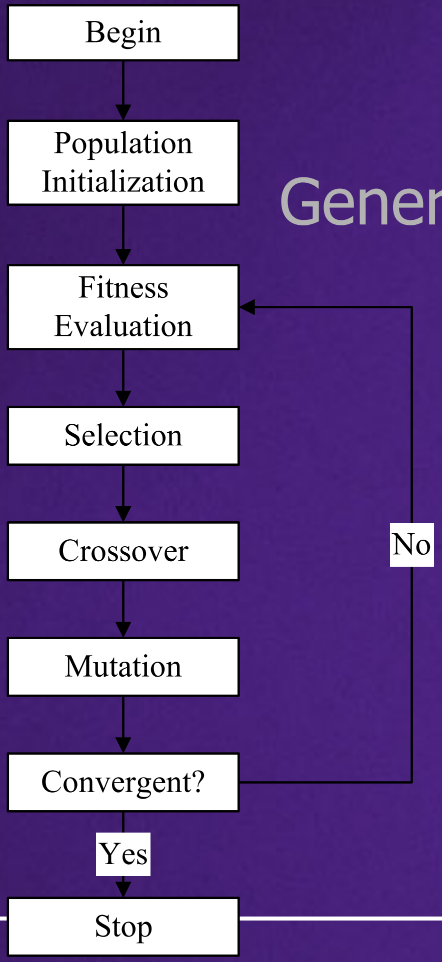
Flowsheet Optimization:
Scaled Gradient Analysis (SGA):

	Design variable	Unit	Incremental change	Scale factor
1	Change the **recovery** of MA in the **absorber**	unitless	0.01	0.1
2	Increase the **solvent** inlet temperature in **absorber**	ºC	5	10
3	Change **recovery** of MA in the **distillation column**	unitless	0.018	0.1
4	Change the **feed ratio** of air to n-butane	unitless	5	10
5	Change the **reactor pressure**	kPa	10	30
6	Change the **reaction temperature**	ºC	5	20
7	Change **reflux ratio** in **distillation column**	unitless	0.1	0.5
8	Change **minimum approach temperature** of **heat exchanger** between reactor feed and off-gas	ºC	5	10
9	Change **minimum approach temperature** of **heat exchanger** between recycle solvent and distillation feed	ºC	5	10

Optimization using the Genetic Algorithm

Chen, H., Rogers, T.N., Barna, B.A., Shonnard, D.R.,, *Environmental Progress*, in press April, 2003.

Flowsheet Optimization:
Genetic Algorithm



Begin

Population Initialization

Fitness Evaluation

Selection

Crossover

Mutation

Convergent?

No

Yes

Stop

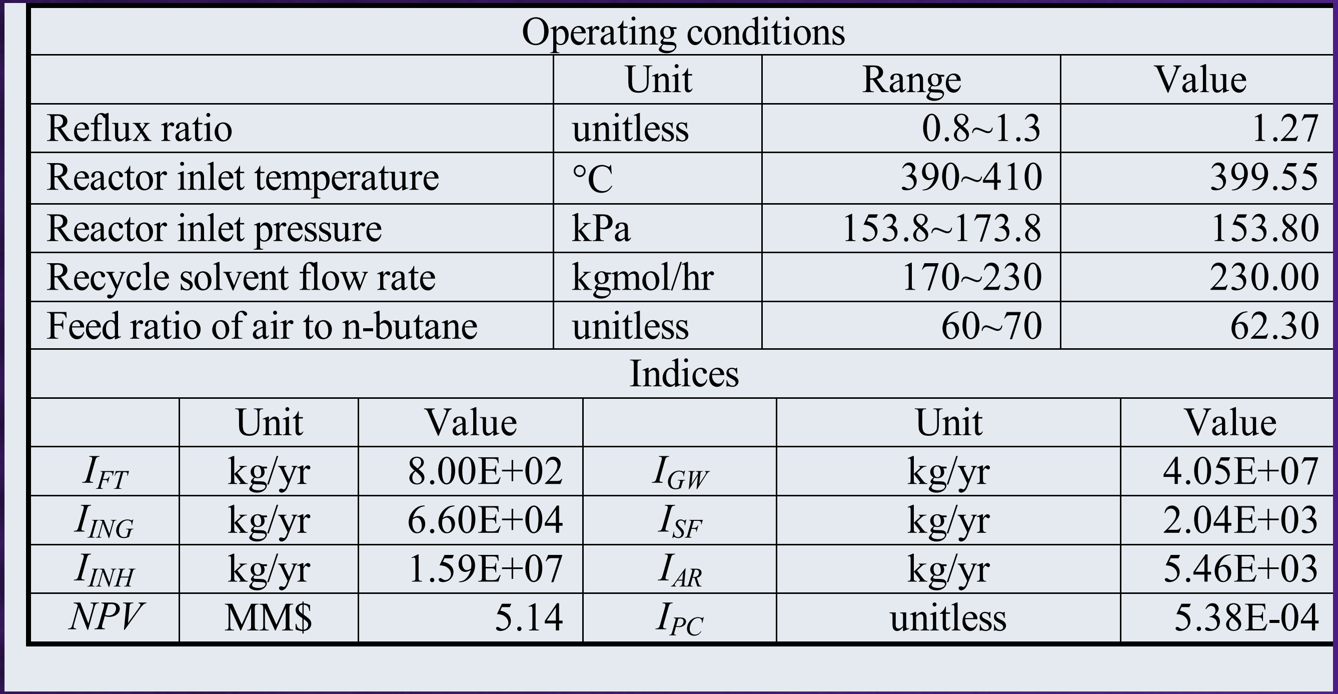
Generations, 100

Population Size, 100

Mutation Probability, 0.04

Optimization Results: n-butane Process

AHP Ranking is the Objective Function



Operating conditions

	Unit	Range	Value
Reflux ratio	unitless	0.8~1.3	1.27
Reactor inlet temperature	°C	390~410	399.55
Reactor inlet pressure	kPa	153.8~173.8	153.80
Recycle solvent flow rate	kgmol/hr	170~230	230.00
Feed ratio of air to n-butane	unitless	60~70	62.30

Indices

	Unit	Value		Unit	Value
I_{FT}	kg/yr	8.00E+02	I_{GW}	kg/yr	4.05E+07
I_{ING}	kg/yr	6.60E+04	I_{SF}	kg/yr	2.04E+03
I_{INH}	kg/yr	1.59E+07	I_{AR}	kg/yr	5.46E+03
NPV	MM$	5.14	I_{PC}	unitless	5.38E-04

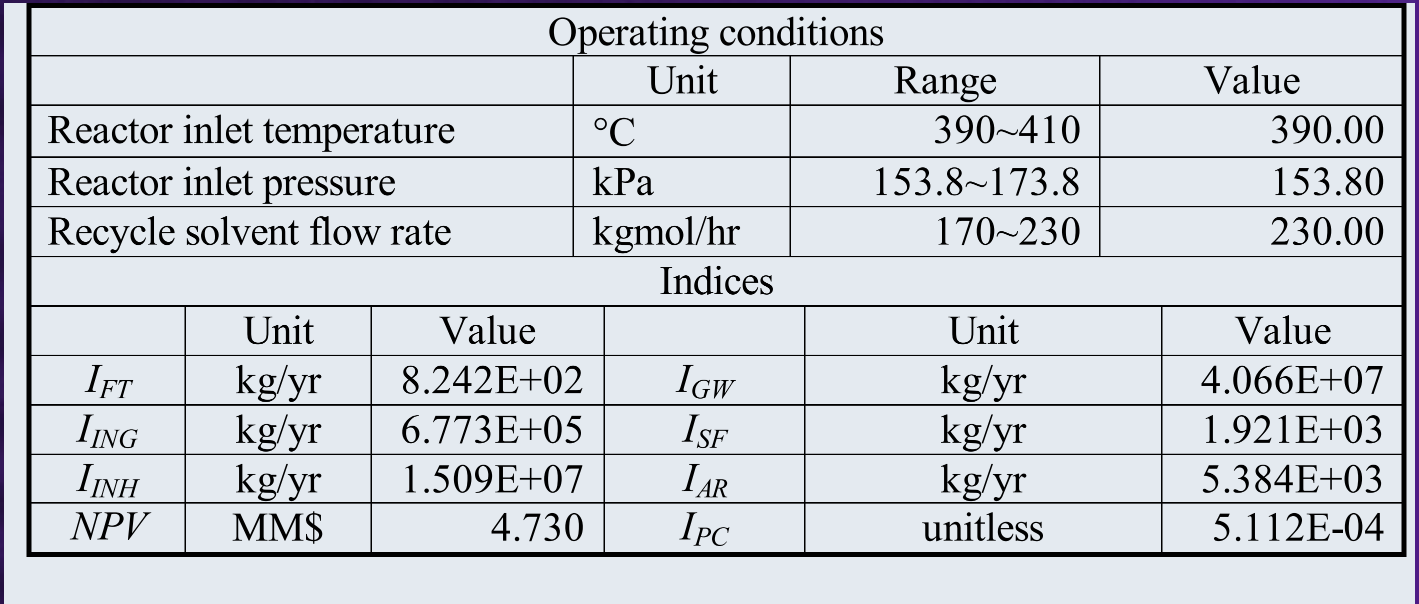
Optimization Results: n-butane Process

NPV is the Objective Function

<table>
<tr><th colspan="6">Operating conditions</th></tr>
<tr><td colspan="2">inlet temperature</td><td>°C</td><td colspan="2">390~410</td><td>399.08</td></tr>
<tr><td colspan="2">Reactor inlet pressure</td><td>kPa</td><td colspan="2">153.8~173.8</td><td>153.80</td></tr>
<tr><td colspan="2">Recycle solvent flow rate</td><td>kgmol/hr</td><td colspan="2">170~230</td><td>230.00</td></tr>
<tr><td colspan="2">Feed ratio of air to n-butane</td><td>unitless</td><td colspan="2">60~70</td><td>62.10</td></tr>
<tr><th colspan="6">Indices</th></tr>
<tr><td></td><td>Unit</td><td>Value</td><td></td><td>Unit</td><td>Value</td></tr>
<tr><td>I_{FT}</td><td>kg/yr</td><td>8.01E+02</td><td>I_{GW}</td><td>kg/yr</td><td>4.05E+07</td></tr>
<tr><td>I_{ING}</td><td>kg/yr</td><td>6.61E+05</td><td>I_{SF}</td><td>kg/yr</td><td>2.04E+03</td></tr>
<tr><td>I_{INH}</td><td>kg/yr</td><td>1.60E+07</td><td>I_{AR}</td><td>kg/yr</td><td>5.48E+03</td></tr>
<tr><td>*NPV*</td><td>MM$</td><td>5.14</td><td>$I_{PC}$</td><td>Unitless</td><td>5.40E-04</td></tr>
</table>

Optimization Results: n-butane Process

I_{PC} is the Objective Function



Operating conditions

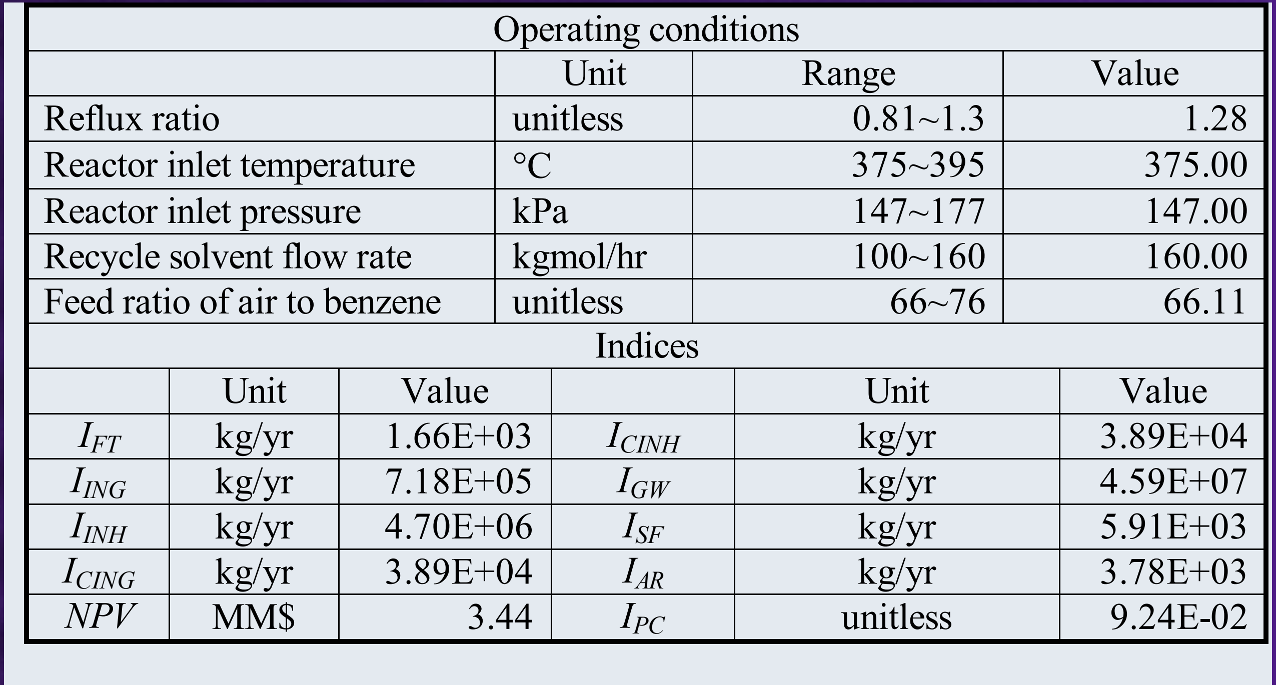
	Unit	Range	Value
Reactor inlet temperature	°C	390~410	390.00
Reactor inlet pressure	kPa	153.8~173.8	153.80
Recycle solvent flow rate	kgmol/hr	170~230	230.00

Indices

	Unit	Value		Unit	Value
I_{FT}	kg/yr	8.242E+02	I_{GW}	kg/yr	4.066E+07
I_{ING}	kg/yr	6.773E+05	I_{SF}	kg/yr	1.921E+03
I_{INH}	kg/yr	1.509E+07	I_{AR}	kg/yr	5.384E+03
NPV	MM$	4.730	I_{PC}	unitless	5.112E-04

Optimization Results: Benzene Process

AHP Ranking is the Objective Function

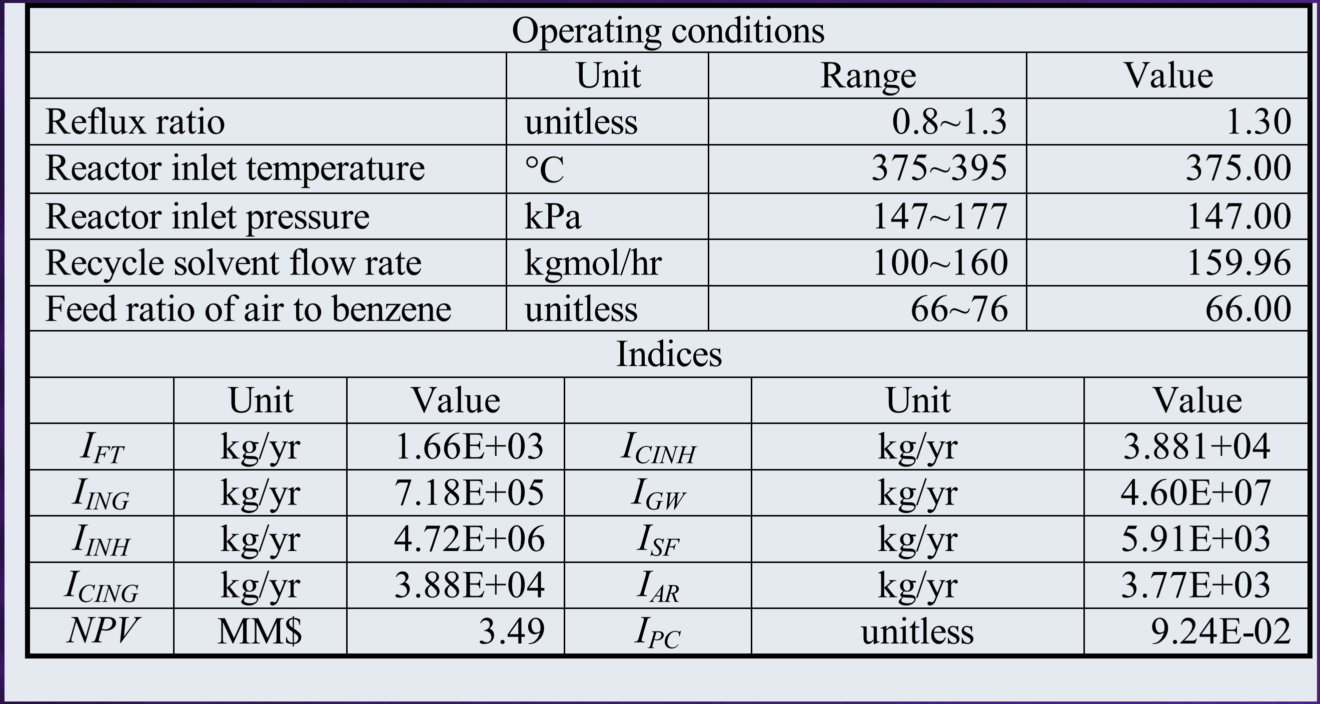


<table>
<tr><th colspan="4">Operating conditions</th></tr>
<tr><th></th><th>Unit</th><th>Range</th><th>Value</th></tr>
<tr><td>Reflux ratio</td><td>unitless</td><td>0.81~1.3</td><td>1.28</td></tr>
<tr><td>Reactor inlet temperature</td><td>°C</td><td>375~395</td><td>375.00</td></tr>
<tr><td>Reactor inlet pressure</td><td>kPa</td><td>147~177</td><td>147.00</td></tr>
<tr><td>Recycle solvent flow rate</td><td>kgmol/hr</td><td>100~160</td><td>160.00</td></tr>
<tr><td>Feed ratio of air to benzene</td><td>unitless</td><td>66~76</td><td>66.11</td></tr>
</table>

<table>
<tr><th colspan="6">Indices</th></tr>
<tr><th></th><th>Unit</th><th>Value</th><th></th><th>Unit</th><th>Value</th></tr>
<tr><td>I_{FT}</td><td>kg/yr</td><td>1.66E+03</td><td>I_{CINH}</td><td>kg/yr</td><td>3.89E+04</td></tr>
<tr><td>I_{ING}</td><td>kg/yr</td><td>7.18E+05</td><td>I_{GW}</td><td>kg/yr</td><td>4.59E+07</td></tr>
<tr><td>I_{INH}</td><td>kg/yr</td><td>4.70E+06</td><td>I_{SF}</td><td>kg/yr</td><td>5.91E+03</td></tr>
<tr><td>I_{CING}</td><td>kg/yr</td><td>3.89E+04</td><td>I_{AR}</td><td>kg/yr</td><td>3.78E+03</td></tr>
<tr><td>*NPV*</td><td>MM$</td><td>3.44</td><td>$I_{PC}$</td><td>unitless</td><td>9.24E-02</td></tr>
</table>

Optimization Results: Benzene Process

NPV is the Objective Function



Operating conditions

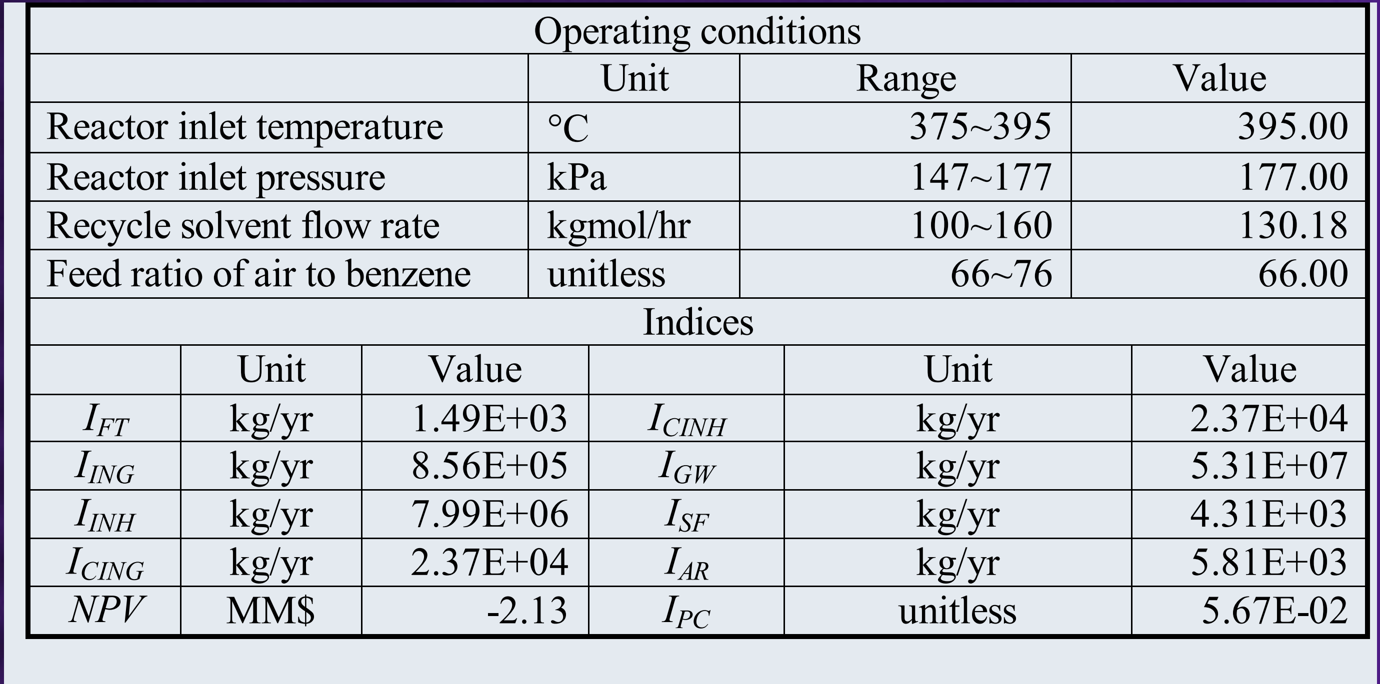
	Unit	Range	Value
Reflux ratio	unitless	0.8~1.3	1.30
Reactor inlet temperature	°C	375~395	375.00
Reactor inlet pressure	kPa	147~177	147.00
Recycle solvent flow rate	kgmol/hr	100~160	159.96
Feed ratio of air to benzene	unitless	66~76	66.00

Indices

	Unit	Value		Unit	Value
I_{FT}	kg/yr	1.66E+03	I_{CINH}	kg/yr	3.881+04
I_{ING}	kg/yr	7.18E+05	I_{GW}	kg/yr	4.60E+07
I_{INH}	kg/yr	4.72E+06	I_{SF}	kg/yr	5.91E+03
I_{CING}	kg/yr	3.88E+04	I_{AR}	kg/yr	3.77E+03
NPV	MM$	3.49	I_{PC}	unitless	9.24E-02

Optimization Results: Benzene Process

I_{PC} is the Objective Function



Operating conditions

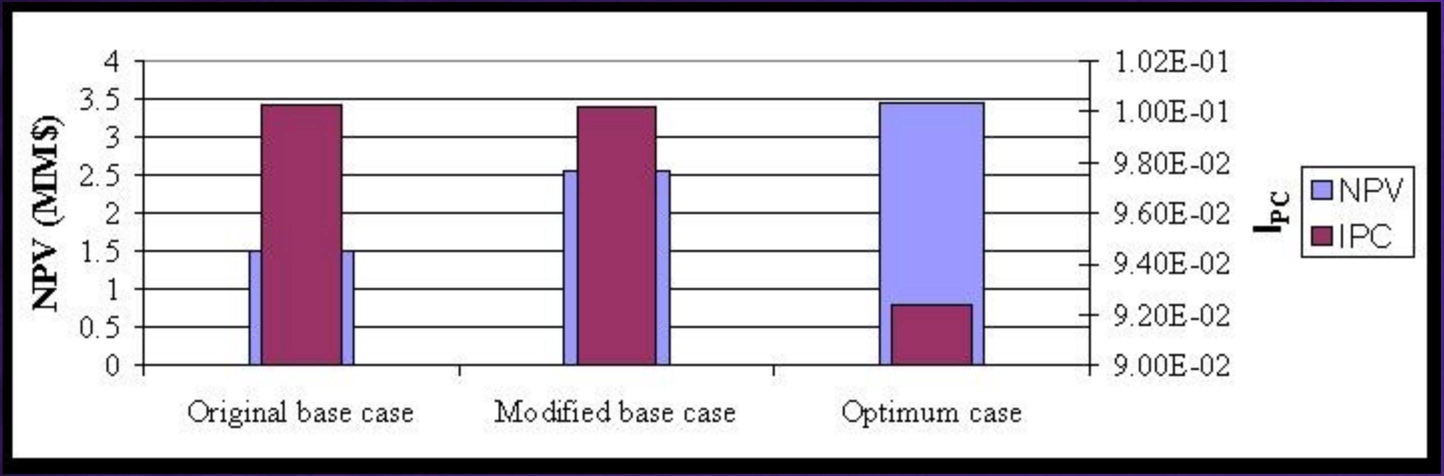
	Unit	Range	Value
Reactor inlet temperature	°C	375~395	395.00
Reactor inlet pressure	kPa	147~177	177.00
Recycle solvent flow rate	kgmol/hr	100~160	130.18
Feed ratio of air to benzene	unitless	66~76	66.00

Indices

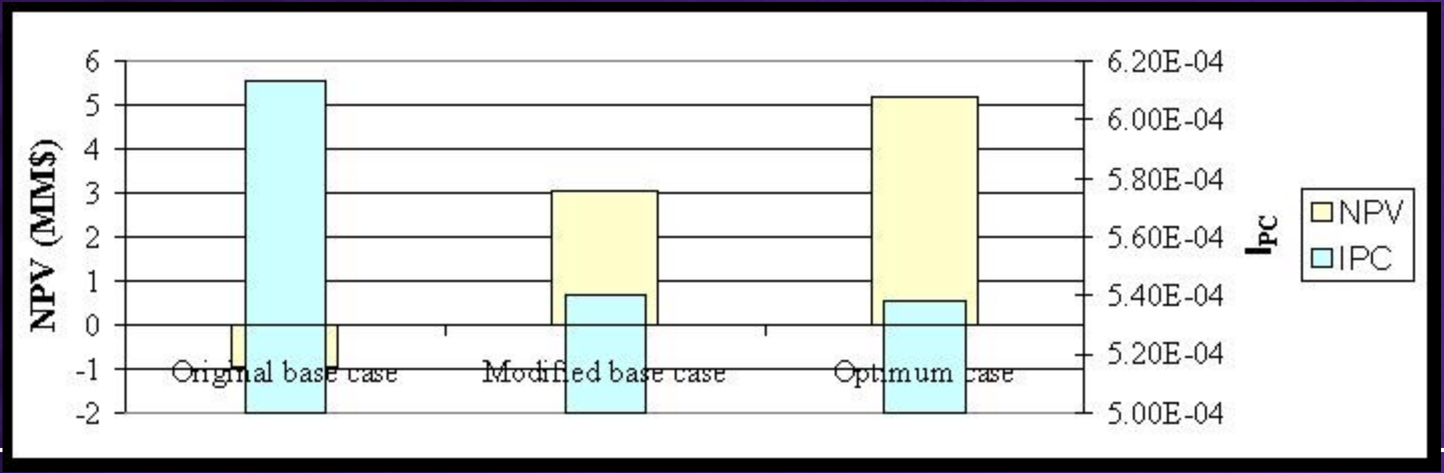
	Unit	Value		Unit	Value
I_{FT}	kg/yr	1.49E+03	I_{CINH}	kg/yr	2.37E+04
I_{ING}	kg/yr	8.56E+05	I_{GW}	kg/yr	5.31E+07
I_{INH}	kg/yr	7.99E+06	I_{SF}	kg/yr	4.31E+03
I_{CING}	kg/yr	2.37E+04	I_{AR}	kg/yr	5.81E+03
NPV	MM$	-2.13	I_{PC}	unitless	5.67E-02

Continuous Improvement of Design Performance

benzene process design



n-butane process design



Summary / Conclusions

- A *systematic* and *hierarchical* approach for EC-D of chemical processes is shown.
- The EC-D approach is applied to a case study design for MA production from either benzene or n-butane.
- A number of computer-aided tools are available to facilitate EC-D.
- This approach yields a continuous improvement in both economic and environmental performance through the designs process.
- Early design assessment methods are validated using detailed design and optimization results.

Acknowledgements

- EPA Contract 3W-0500-NATA – OPPT, Green Engineering Program
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