Green Chemistry:
Evaluation of Alternative Reaction Pathways
Chapters 7 and 8

David R. Shonnard
Department of Chemical Engineering
Michigan Technological University

Organizational Structure of the GE Textbook:

A Hierarchy of Design Activity

Design Stage	***P2 Tools***	***Environmental Evaluation***	***Book Chapter***
1. Reaction pathways, conversions, and yields, raw materials, solvents	• Green Chemistry • atom efficiency	Tier 1 (simplified)	7, 8
2. Flowsheet systhesis, specific process units defined	Release estimation, optimum choice of • mass separating agents • process units • processing conditions	Tier 2 (intermediate)	8, 9
3. Detailed design	• Process integration methods • multimedia environmental fate modeling • environmental impact assessment	Tier 3 (more rigerous)	10, 11

Outline

The selection of a reaction pathway is the key step to establish the environmental performance of a chemical process, affecting the downstream separation units and their energy requirements, emissions, and impacts.

- Educational goals and topics covered in the module
- Green Chemistry (Chapter 7) and
- assessing potential environmental impacts based on limited information (Chapter 8)

Educational goals and topics covered in the module

Students will:

- understand a “Tier 1” approach for chemical process environmental evaluation
- learn qualitative and quantitative approaches to Green Chemistry
- be able to evaluate alternative reaction pathways; both economically and environmentally.

Green Chemistry - Ch 7

- Guiding principles for Green Chemistry
  - Maximum incorporation of raw materials into final products
  - All chemicals should be nontoxic yet functional
  - Auxiliary substances (solvents) should be nontoxic
  - High energy efficiency
  - Use of renewable resources is recommended
  - Recyclable reagents and raw materials
  - End products should not persist in the environment

Anastas, P.T. and Warner, J.C. 1998, Green Chemistry: Theory and Practice, Oxford University Press, New York

---

Feedstocks and solvents

- Important considerations
  - Human / ecosystem health properties
    - Bioaccumulative?
    - Persistent?
    - Toxic?
    - Global warming, Ozone depletion, Smog formation?
    - Flammable or otherwise hazardous?
    - Renewable or non renewable resource?
  - Life cycle environmental burdens? - Ch 13, 14

Synthesis pathways

Reaction Type	***Waste Generation Potential***
Addition Reaction Isobutylene + methanol → methyl tert-butyl ether $C_4H_8 + CH_3OH \rightarrow (C_4H_9)\text{-}O\text{-}CH_3$	• completely incorporate starting material into product
Substitution Reaction Phenol + ammonia → analine + water $C_6H_5\text{-}OH + NH_3 \rightarrow C_6H_5\text{-}NH_2 + H_2O$	• stoichiometric amounts of waste are generated
Elimination Reaction Ethylbenzene → styrene + hydrogen $C_6H_5\text{-}C_2H_5 \rightarrow C_6H_5\text{-}C_2H_3 + H_2$	• stoichiometric amounts of waste are generated

---

Atom and mass efficiency:
magnitude of improvements possible

Atom Efficiency

- the fraction of starting material incorporated into the desired product -

$C_6H_5\text{-}OH + NH_3 \rightarrow C_6H_5\text{-}NH_2 + H_2O$

- Carbon - 100%
- Hydrogen - 7/9 x 100 = 77.8%
- Oxygen - 0/1 x 100 = 0%
- Nitrogen - 100%

Mass Efficiency (Basis 1 mole of product)

$C_6H_5\text{-}OH + NH_3 \rightarrow C_6H_5\text{-}NH_2 + H_2O$

Mass in Product = (6 C)(12) + (7 H)(1) + (0 O)(16) + (1 N)(14) = 93 grams

Mass in Reactants = (6 C)(12) + (9 H)(1) + (1 O)(16) + (1 N)(14) = 111 grams

Mass Efficiency = 93/111 x 100 = 83.8%

Chapter 7: Adipic Acid Synthesis
Traditional vs. New

Traditional Route - from cyclohexanol/cyclohexanone

$$C_6H_{12}O + 2\ HNO_3 + 2\ H_2O \xrightarrow[V\ (.02\text{-}.1\%)]{Cu\ (.1\text{-}.5\%)} C_6H_{10}O_4 + (NO,\ NO_2,\ N_2O,\ N_2)$$

hazardous

global warming
ozone depletion

92-96% Yield of Adipic Acid

- Carbon - 100%
- Oxygen - 4/9 x 100 = 44.4%
- Hydrogen - 10/18 x 100 = 55.6%
- Nitrogen - 0%

Product Mass = (6 C)(12) + (10 H)(1) + (4 O)(16) = 146 g

Reactant Mass = (6 C)(12) + (18 H)(1) + (9 O)(16) + (2 N)(14) = 262 g

Mass Efficiency = 146/262 x 100 = **55.7%**

Davis and Kemp, 1991, Adipic Acid, in Kirk-Othmer Encyclopedia of Chemical Technology, V. 1, 466 - 493

Chapter 7: Adipic Acid Synthesis
Traditional vs. New

New Route - from cyclohexene

$$C_6H_{10} + 4\ H_2O_2 \xrightarrow[{[CH_3(n\text{-}C_8H_{17})_3N]HSO_4\ (1\%)}]{Na_2WO_4\bullet 2H_2O\ (1\%)} C_6H_{10}O_4 + 4\ H_2O$$

90% Yield of Adipic Acid

- Carbon - 100%
- Oxygen - 4/8 x 100 = 50%
- Hydrogen - 10/18 x 100 = 55.6%

Product Mass = (6 C)(12) + (10 H)(1) + (4 O)(16) = 146 g

Reactant Mass = (6 C)(12) + (18 H)(1) + (8 O)(16) = 218 g

Mass Efficiency = 146/218 x 100 = 67%

Sato, et al. 1998, A "green" route to adipic acid:…, Science, V. 281, 11 Sept. 1646 - 1647

Maleic anhydride (MA) synthesis: benzene vs butane - mass efficiency

Benzene Route (Hedley et al. 1975, reference in ch. 8)

$$2\,C_6H_6 + \underset{\text{(air)}}{9\,O_2} \xrightarrow[MoO_3]{V_2O_5} 2\,C_4H_2O_3 + H_2O + 4\,CO_2$$

70% Yield of Maleic Anhydride from Benzene in Fixed Bed Reactor

Mass Efficiency =

Butane Route

$$C_4H_{10} + \underset{\text{(air)}}{3.5\,O_2} \xrightarrow{(VO)_2P_2O_5} C_4H_2O_3 + 4\,H_2O$$

60% Yield of Maleic Anhydride from Butane in Fixed Bed Reactor

Mass Efficiency =

Felthouse et al., 1991, "Maleic Anhydride, ..", in Kirk-Othmer Encyclopedia of Chemical Technology, V. 15, 893 - 928

Maleic anhydride (MA) synthesis: benzene vs butane - summary table

Chapter 8 Material	**Stoichiometry** [1]	**$/lb** [2]	**TLV** [3]	**TW** [4]	**Persistence** [5]		**log BCF** [5]
					Air (d)	**Water (d)**	
Benzene Process							
Benzene [71-43-2]	-1.19	0.184	10	100	10	10	1.0
Maleic Anhydride	1.00	0.530	0.25	----	1.7	7×10^{-4}	----
Butane Process							
Butane [106-97-8]	-1.22	0.141	800	----	7.25	----	----
Maleic Anhydride	1.00	0.530	0.25	----	1.7	7×10^{-4}	----

1 Rudd et al. 1981, "Petroleum Technology Assessment", Wiley Interscience, New York
2 Chemical Marketing Reporter (Benzene and MA 6/12/00); Texas Liquid (Butane 6/22/00)
3 Threshold Limit Value, ACGIH - Amer. Conf. of Gov. Indust. Hyg., Inc. , www.acgih.org
4 Toxicity Weight, www.epa.gov/opptintr/env_ind/index.html and www.epa.gov/ngispgm3/iris/subst/index.html
5 ChemFate Database - www.esc.syrres.com, EFDB menu item

Maleic anhydride (MA) synthesis: benzene vs butane - tier 1 assessment

(TLV Index)

$$\text{Environmental Index (non-carcinogenic)} = \sum_i |\nu_i| \times (\text{TLV}_i)^{-1}$$

Benzene Route

TLV Index = ?

Butane Route

TLV Index = ?

Where ν_i is the overall stoichiometric coefficient of reactant or product *i*

Maleic anhydride (MA) synthesis: benzene vs butane - tier 1 assessment

EPA Index

$$\text{Environmental Index (carcinogenic)} = \sum_i |\nu_i| \times (\texttt{Maximum toxicity we}$$

Benzene Route

EPA Index = ?

Butane Route

EPA Index = ?

A More Detailed Analysis of 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

Maleic anhydride (MA) production: 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) = 0.0313 \$/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

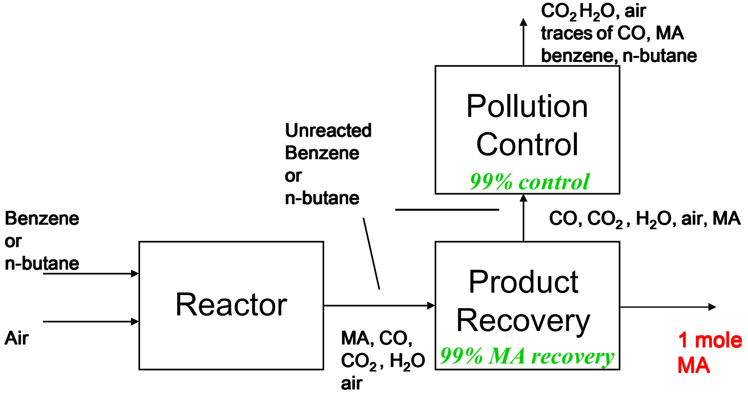
MA Yield | nC4 MW | nC4 cost

Assumption: raw material costs dominate total cost of the process

MA production: IO assumptions

Level 1. Input / Output Information

"Tier 1" Environmental Impact Analysis



Maleic Anhydride Synthesis
Benzene vs Butane - Tier 1 Assessment

Benzene Exiting Reactor:

$(1\text{mole}/((0.70)(.99)) \times (1-0.95) = 0.0722 \text{ mole benzene/mole of MA}$

Benzene Emission from Pollution Control:

$(0.01) \times (0.0722 \text{ mole/mole of MA}) = \boxed{7.22\text{x}10^{-4}} \text{ mole benzene/mole of MA}$

n-Butane Exiting Reactor:

$(1\text{mole}/((0.60)(.99)) \times (1-0.85) = 0.2525 \text{ mole n-butane/mole of MA}$

n-Butane Emission from Pollution Control:

$(0.01) \times (0.2525 \text{ mole/mole of MA}) = \boxed{2.53\text{x}10^{-3}} \text{ mole n-butane/mole of MA}$

Maleic Anhydride Synthesis
Benzene vs Butane - Tier 1 Assessment

Benzene Process : CO Exiting Reactor :

$$(1\,\text{mole}/((0.70)(.99))\times(0.95-0.7)\times\frac{6}{2}=1.082\,\frac{\text{mole CO}}{\text{mole MA}}$$

Benzene Process : CO Emission from Pollution Control :

$$(0.01)\times(1.082\text{ mole/mole of MA})=\boxed{1.08\text{x}10^{-2}\,\frac{\text{mole CO}}{\text{mole MA}}}$$

n - Butane Process : CO Exiting Reactor :

$$(1\,\text{mole}/((0.60)(.99))\times(0.85-0.6)\times\frac{4}{2}=0.842\,\frac{\text{mole CO}}{\text{mole MA}}$$

n - Butane Process : CO Emission from Pollution Control :

$$(0.01)\times(0.842\text{ mole/mole of MA})=\boxed{8.42\text{x}10^{-3}\,\frac{\text{mole CO}}{\text{mole MA}}}$$

Chapter 8: Maleic Anhydride Synthesis
Benzene vs Butane - Tier 1 Assessment

Benzene Process : CO_2 Exiting Reactor :

$$(1\,\text{mole MA})(\frac{2\text{ mole }CO_2}{\text{mole MA}})+(1\,\text{mole}/((0.7)(.99))\times(0.95-0.7)\times\frac{6}{2}=3.082\,\frac{\text{mole }CO_2}{\text{mole MA}}$$

Benzene Process : CO_2 Emission from Pollution Control :

$$(3.082)+(0.99)(1.082)+(0.99)(0.0722)(6)+(0.01)(0.99)(4)=\boxed{4.622\,\frac{\text{mole }CO_2}{\text{mole MA}}}$$

n - Butane Process : CO_2 Exiting Reactor :

$$(1\,\text{mole}/((0.60)(.99))\times(0.85-0.6))\times\frac{4}{2}=0.842\,\frac{\text{mole }CO_2}{\text{mole MA}}$$

n - Butane Process : CO_2 Emission from Pollution Control :

$$(0.842)+(0.99)(0.842)+(0.99)(0.25)(4)+(0.01)(0.99)(4)=\boxed{2.705\,\frac{\text{mole }CO_2}{\text{mole MA}}}$$

MA production: Flows/Emissions for process streams

Benzene process					
	Flow Rates/Emissions (kg/mole of MA)				
	Benzene	CO	CO_2	Maleic anhydride	Total
Reactor inlet	1.13E-01	0.00E+00	0.00E+00	0.00E+00	1.13E-01
Reactor outlet	5.63E-03	3.03E-02	1.36E-01	9.90E-02	2.71E-01
Separation unit (w/pollution control)	5.63E-05	3.03E-04	2.03E-01	9.90E-06	2.03E-01
n-Butane process					
	Flow Rates/Emissions (kg/mole of MA)				
	n-Butane	CO	CO_2	Maleic anhydride	Total
Reactor inlet	9.76E-02	0.00E+00	0.00E+00	0.00E+00	9.76E-02
Reactor outlet	1.46E-02	2.36E-02	3.71E-02	9.90E-02	1.74E-01
Separation unit (w/pollution control)	1.46E-04	2.36E-04	1.19E-01	9.90E-06	1.19E-01

MA production: Flows/Emissions for process streams

Benzene process					
	Flow Rates/Emissions (kg/mole of MA)				
	Benzene	CO	CO_2	Maleic anhydride	Total
Reactor inlet	1.13E-01	0.00E+00	0.00E+00	0.00E+00	1.13E-01
Reactor outlet	5.63E-03	3.03E-02	1.36E-01	9.90E-02	2.71E-01
Separation unit (w/pollution control)	5.63E-05	3.03E-04	2.03E-01	9.90E-06	2.03E-01
n-Butane process					
	Flow Rates/Emissions (kg/mole of MA)				
	n-Butane	CO	CO_2	Maleic anhydride	Total
Reactor inlet	9.76E-02	0.00E+00	0.00E+00	0.00E+00	9.76E-02
Reactor outlet	1.46E-02	2.36E-02	3.71E-02	9.90E-02	1.74E-01
Separation unit (w/pollution control)	1.46E-04	2.36E-04	1.19E-01	9.90E-06	1.19E-01

MA production: Flows/Emissions for process streams

Benzene process					
	Flow Rates/Emissions (kg/mole of MA)				
	Benzene	CO	CO_2	Maleic anhydride	Total
Reactor inlet	1.13E-01	0.00E+00	0.00E+00	0.00E+00	1.13E-01
Reactor outlet	5.63E-03	3.03E-02	1.36E-01	9.90E-02	2.71E-01
Separation unit (w/pollution control)	5.63E-05	3.03E-04	2.03E-01	9.90E-06	2.03E-01
n-Butane process					
	Flow Rates/Emissions (kg/mole of MA)				
	n-Butane	CO	CO_2	Maleic anhydride	Total
Reactor inlet	9.76E-02	0.00E+00	0.00E+00	0.00E+00	9.76E-02
Reactor outlet	1.46E-02	2.36E-02	3.71E-02	9.90E-02	1.74E-01
Separation unit (w/pollution control)	1.46E-04	2.36E-04	1.19E-01	9.90E-06	1.19E-01

MA production: Flows/Emissions for process streams

Benzene process					
	Flow Rates/Emissions (kg/mole of MA)				
	Benzene	CO	CO_2	Maleic anhydride	Total
Reactor inlet	1.13E-01	0.00E+00	0.00E+00	0.00E+00	1.13E-01
Reactor outlet	5.63E-03	3.03E-02	1.36E-01	9.90E-02	2.71E-01
Separation unit (w/pollution control)	5.63E-05	3.03E-04	2.03E-01	9.90E-06	2.03E-01
n-Butane process					
	Flow Rates/Emissions (kg/mole of MA)				
	n-Butane	CO	CO_2	Maleic anhydride	Total
Reactor inlet	9.76E-02	0.00E+00	0.00E+00	0.00E+00	9.76E-02
Reactor outlet	1.46E-02	2.36E-02	3.71E-02	9.90E-02	1.74E-01
Separation unit (w/pollution control)	1.46E-04	2.36E-04	1.19E-01	9.90E-06	1.19E-01

Recap:
Tier 1 Environmental Assessment

- A rapid screening assessment of reaction pathways
- Toxicity indices are included, with supplemental information on environmental fate and persistence
- Emission estimates were added for an overall flowsheet comparison
- More complete emissions inventory is needed as well as environmental fate and impact assessment

---

Emission Factors -
for major equipment

Page 223 of textbook

$E = m_{VOC} EF_{av} M$ Equation 8-4

Average Emission Factors for Chemical Process Units Calculated from the US EPA L&E Database

Process Unit	EF_{av} **(kg emitted/10^3 kg throughput)**
Reactor Vents	1.50
Distillation Columns Vents	0.70
Absorber Units	2.20
Stripping Columns	0.20
Sumps/Decanters	0.02
Dryers	0.70
Cooling Towers	0.10

Recap

Green Chemistry concepts and Atom Economy are useful for designing more environmentally beneficial reaction pathways. Early design Green Engineering analysis methods for environmental impacts of alternatives.

- Educational goals and topics covered in the module
- Green Chemistry (Chapter 7) and assessing potential impacts based on limited information (Chapter 8)
- Estimating emissions from processes in early design.