



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

David R. Shonnard
Department of Chemical Engineering
Michigan Technological University



Michigan Technological University

1

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.***

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



Michigan Technological University

2

Educational goals and topics covered in the module



Students will:

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

Green Chemistry - Ch 7



- 1 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



1 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



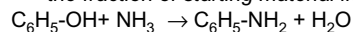
Reaction Type	Waste Generation Potential
Addition Reaction Isobutylene + methanol → methyl tert-butyl ether $C_4H_8 + CH_3OH \rightarrow (C_4H_9)-O-CH_3$	• completely incorporate starting material into product
Substitution Reaction Phenol + ammonia → aniline + water $C_6H_5-OH + NH_3 \rightarrow C_6H_5-NH_2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

Atom and mass efficiency: magnitude of improvements possible



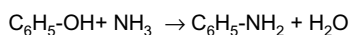
Atom Efficiency

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



- Carbon - 100%
- Hydrogen - $7/9 \times 100 = 77.8\%$
- Oxygen - $0/1 \times 100 = 0\%$
- Nitrogen - 100%

Mass Efficiency (Basis 1 mole of product)



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

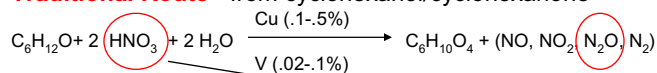
Mass in Reactants = (6 C)(12) + (9 H)(1) + (1 O)(16) + (1 N)(14) = 111 grams

Mass Efficiency = $93/111 \times 100 = 83.8\%$

Chapter 7: Adipic Acid Synthesis Traditional vs. New



Traditional Route - from cyclohexanol/cyclohexanone



92-96% Yield of Adipic Acid

hazardous

global warming
ozone depletion

- Carbon - 100%
- Oxygen - $4/9 \times 100 = 44.4\%$
- Hydrogen - $10/18 \times 100 = 55.6\%$
- 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

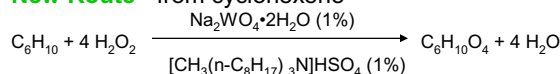
Mass Efficiency = $146/262 \times 100 = 55.7\%$

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



90% Yield of Adipic Acid

- Carbon - 100%
- Oxygen - $4/8 \times 100 = 50\%$
- Hydrogen - $10/18 \times 100 = 55.6\%$

Product Mass = $(6 \text{ C})(12) + (10 \text{ H})(1) + (4 \text{ O})(16) = 146 \text{ g}$

Reactant Mass = $(6 \text{ C})(12) + (18 \text{ H})(1) + (8 \text{ O})(16) = 218 \text{ g}$

Mass Efficiency = $146/218 \times 100 = 67\%$

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

MichiganTech

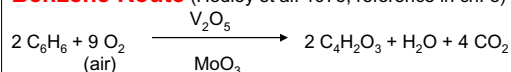
Michigan Technological University

9

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



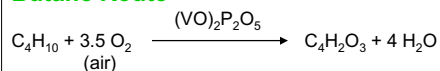
Benzene Route (Hedley et al. 1975, reference in ch. 8)



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

$$\text{Mass Efficiency} = \frac{2(4)(12) + 3(2)(16) + 2(2)(1)}{2(6)(12) + 9(2)(16) + 2(6)(1)} (100) = 44.4\%$$

Butane Route



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

$$\text{Mass Efficiency} = \frac{(4)(12) + (3)(16) + (2)(1)}{(4)(12) + 3.5(2)(16) + (10)(1)} (100) = 57.6\%$$

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

MichiganTech

Michigan Technological University

10

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	7x10 ⁻⁴	----
Butane Process							
Butane [106-97-8]	-1.22	0.141	800	----	7.25	----	----
Maleic Anhydride	1.00	0.530	0.25	----	1.7	7x10 ⁻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/inv_ind/index.html and www.epa.gov/ngispgm3/liris/subst/index.html

⁵ ChemFate Database - www.esc.syrres.com, EFDB menu item



Michigan Technological University

11

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



(TLV Index)

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

Benzene Route

$$\text{TLV Index} = (1.19)(1/10) + (1.0)(1/.25) = 4.12$$

Butane Route

$$\text{TLV Index} = (1.22)(1/800) + (1.0)(1/.25) = 4.00$$

Where v_i is the overall stoichiometric coefficient of reactant or product i



Michigan Technological University

12

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



EPA Index

Environmental Index (carcinogenic) = $\sum_i |v_i| \times (\text{Maximum toxicity weight})$

Benzene Route

$$\text{EPA Index} = (1.19)(100) + (1.0)(0) = 119$$

Butane Route

$$\text{EPA Index} = (1.22)(0) + (1.0)(0) = 0$$



Michigan Technological University

13

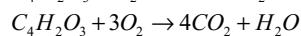
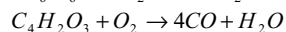
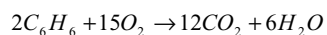
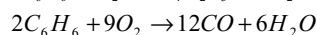
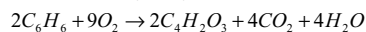
A More Detailed Analysis of MA Production



Level 1. Input / Output Information

Benzene Process

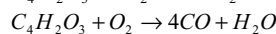
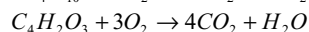
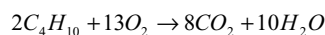
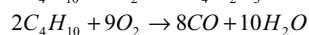
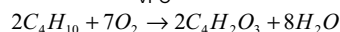
V_2O_5 - MoO_3



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

n-Butane Process

VPO



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



Michigan Technological University

14

Maleic anhydride (MA) production: Costs



Level 1. Input / Output Information

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

Benzene Process

$$1 \text{ mole} / (0.70 \text{ mole}) \times (78 \text{ g/mole}) \times (0.00028 \text{ \$/g}) = 0.0313 \text{ \$/mole of MA}$$

MA Yield
Bz MW
Benzene cost

N-butane process has lower cost

n-Butane Process

$$1 \text{ mole} / (0.60 \text{ mole}) \times (58 \text{ g/mole}) \times (0.00021 \text{ \$/g}) = 0.0203 \text{ \$/mole of MA}$$

MA Yield
nC4 MW
nC4 cost

Assumption: raw material costs dominate total cost of the process

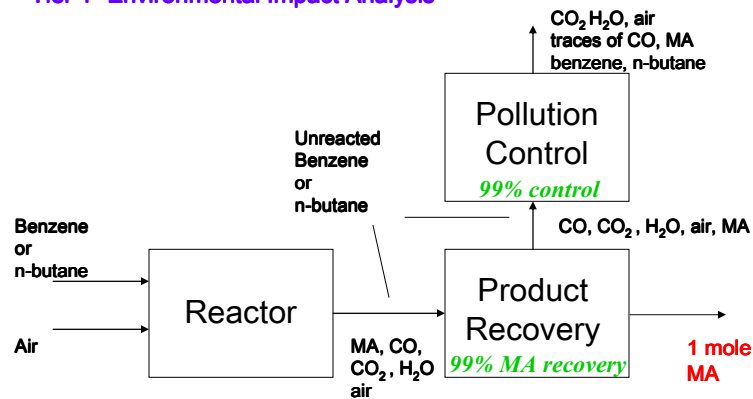


MA production: IO assumptions



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 :

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

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 :

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

MichiganTech

Michigan Technological University

17

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 :

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

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 :

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

MichiganTech

Michigan Technological University

18

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



Benzene Process : CO₂ Exiting Reactor :

$$(1 \text{ mole MA}) \left(\frac{2 \text{ mole CO}_2}{\text{mole MA}} \right) + (1 \text{ mole}) / ((0.7)(.99)) \times (0.95 - 0.7) \times \frac{6}{2} = 3.082 \frac{\text{mole CO}_2}{\text{mole MA}}$$

Benzene Process : CO₂ Emission from Pollution Control :

$$(3.082) + (0.99)(1.082) + (0.99)(0.0722)(6) + (0.01)(0.99)(4) = 4.622 \frac{\text{mole CO}_2}{\text{mole MA}}$$

n-Butane Process : CO₂ 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 : CO₂ Emission from Pollution Control :

$$(0.842) + (0.99)(0.842) + (0.99)(0.25)(4) + (0.01)(0.99)(4) = 2.705 \frac{\text{mole CO}_2}{\text{mole MA}}$$

MichiganTech

Michigan Technological University

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

MichiganTech

Michigan Technological University

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

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

EFRAT program: Add chemicals



Existing: [OK] [Cancel]

Chemicals in Current PFD: [Add] [Delete] [Edit] [Rename] [Save Changes] [Cancel Changes]

Chemicals in Database: [Import This Chemical]

Name
1,1,1-Trichloroethane
1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene
1,2-Dichlorobenzene
1,2-Dichloroethane
1,3-Butadiene
1,3-Dichloropropylene

[Unchanged] [Validated]

MichiganTech

Michigan Technological University

27

EFRAT program: Benzene



Existing: [OK] [Cancel]

Properties of Selected Chemical (Benzene) [Page 1] [Page 2] [Chemical is Valid]

Chemicals in Current PFD: [Add] [Delete] [Edit] [Rename] [Save Changes] [Cancel Changes]

Name	Count
✓ Benzene	7

Chemicals in Database: [Import This Chemical]

Name	Count
Ammonia	7
Anethole(trans)	1
Aniline	1
Anthracene	1
Atrazine	1
Benzene	7
Bisphenol	1

Chemical Link:
 Link with chemical in PFD
 Do not link with chemical in PFD
Chemical Link: []

SMILES String: [n/a]

CAS #: [71-43-2]

Molecular weight, g/gmol:	[78.1]	[Database]
Henry's constant, dm ³ /mol:	[0.216]	[Database]
Octanol-water partition coefficient, dm ³ /mol:	[132]	[Database]
Half-life degradation time in air, hours:	[117]	[Database]
Half-life degradation time in water, days:	[252]	[Database]
Infrared intensity at 300K, (cm ⁻²)(atm ⁻¹):	[Unavailable]	[Database]
Number of carbon atoms in molecule:	[6.00]	[Database]
Atm. singlet oxygen rate, (cm ³)(molecule ⁻¹)(s ⁻¹):	[0]	[Database]
Number of chlorine atoms in molecule:	[0]	[Database]

[Data Changed] [Validated]

MichiganTech

Michigan Technological University

28

EFRAT program: Reactor Emission



Reactor Emissions

Reactor 1 [Save Changes] [OK] [Cancel]

Basic Properties:
 Item Name: Reactor 1
 Enabled for calculations?

Emission Factor:
 Reactor Type: Default
 Emission Factor: 1.50 g/kg
 Service Factor: 100.0%

Flow Rate Parameter (Feed Stream):
 Use flow rate from linked stream
 Use user-entered flow rate
 Flow Rate: 0.112 kg/year
 Link Stream:

Flow Rate Parameter (Product Stream):
 Use flow rate from linked stream
 Use user-entered flow rate
 Flow Rate: 0.269 kg/year
 Link Stream:

Mass Fractions in Reactor Feed Stream:

Chemical	Mass Fraction
Benzene	1
Carbon dioxide	0
Carbon monoxide	0
Maleic Anhydride	0

Mass Fractions in Reactor Product Stream:

Chemical	Mass Fraction
Benzene	0.0207
Carbon dioxide	0.502
Carbon monoxide	0.1115
Maleic Anhydride	0.365

[Unchanged] [Validated]



EFRAT program: Direct Emission



Direct Emissions

[] [OK] [Cancel]

Basic Properties:
 Item Name: Direct 1
 Enabled for calculations?

Flow Rate Parameter:
 Use flow rate from linked stream
 Use user-entered flow rate
 Flow Rate: 0.202 kg/year
 Link Stream:

Mass Fractions in Emission Stream:

Chemical	Mass Fraction
Benzene	0.000276
Carbon dioxide	0.9982
Carbon monoxide	0.00149
Maleic Anhydride	4.86E-005

[Data Changed] [Validated]



EFRAT program: Emissions Window



EFRAT -- C:\DOCUME~1\ADMINI~1\LOCAL5~1\Temp\cpasmdam_temp_1.1\$\$\$\$

Plug-In PFD Tools Help

← Data Changed Validated

All Distillation Tank Reactor Secondary Utility Fugitive Direct Incineration Bracketed column: Units = kg/year

Emissions

Item	Type	[Benzene]	[Carbon dioxide]	[Carbon monoxide]	[Maleic Anhydride]	Status
✓ Direct 1	Direct	5.575E-05	0.2016	3.010E-04	9.817E-05	Validated(uE)
✓ Reactor 1	Reactor	8.818E-05	1.013E-04	2.250E-05	7.364E-05	Validated(uE)

EFRAT program: Viewing Results Emission Summary



Chemical Emission Summary

Edit

Close All emission values are in kg/year

Chemicals	Reactor 1	Direct 1	Total
Benzene	8.818E-005	5.575E-005	0.00014393
Carbon dioxide	0.00010128	0.2016364	0.20173768
Carbon monoxide	2.25E-005	0.00030098	0.00032348
Maleic Anhydride	7.364E-005	9.817E-006	8.345E-005

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.

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