Evaluation of an Improved Phthalic Anhydride Facility

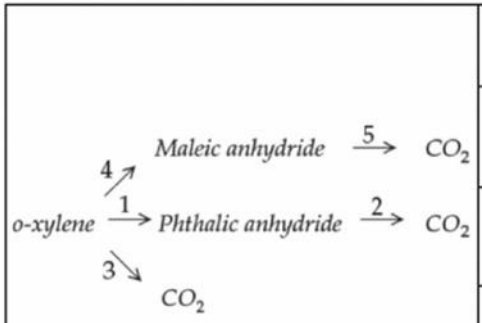
William Lee
Lucas Prescott
Jennifer Silva
Lily Zhong

Objectives

- Design a facility to produce 100,000 metric tonnes/year of Phthalic Anhydride from Ortho-xylene[1]
- Uses of **Phthalic Anhydride**
  - Phthaleins & other dyes
  - Polyester resins (e.g. for paints, lacquers, fiberglass-reinforced plastics)
  - Insecticides
  - Plasticizers e.g. for PVC
- Uses of **Maleic Anhydride**
  - Unsaturated polyester resins (UPSs) fiberglass-reinforced plastics
  - 1,4-butanediol for thermoplastics
  - Hexahydrophthalic anhydrides for epoxy resins
  - Lubricating oil
  - Malic acid for artificial sweetening

1. Bailie, Richard, Whiting, Wallace, Shaeiwitz, Joseph, Turton, Richard, and Bhattacharyya, Debangsu. Analysis, Synthesis, and Design of Chemical Processes, Fifth Edition (2018). Web.

Objectives: Reactions and Kinetics

	1. $C_8H_{10} + 3O_2 \longrightarrow C_8H_4O_3 + 3H_2O$	$r_1 = k_1 p_{xy} p_{O_2}$ $\ln\frac{k_1}{k_0} = -\frac{27{,}000}{RT} + 19.837$
	2. $C_8H_4O_3 + \frac{15}{2}O_2 \longrightarrow 8CO_2 + 2H_2O$	$r_2 = k_2 p_{pa} p_{O_2}$ $\ln\frac{k_2}{k_0} = -\frac{31{,}000}{RT} + 20.86$
	3. $C_8H_{10} + \frac{21}{2}O_2 \longrightarrow 8CO_2 + 5H_2O$	$r_3 = k_3 p_{xy} p_{O_2}$ $\ln\frac{k_3}{k_0} = -\frac{28{,}600}{RT} + 18.97$
	4. $C_8H_{10} + \frac{15}{2}O_2 \longrightarrow C_8H_2O_3 + 4CO_2 + 4H_2O$	$r_4 = k_4 p_{xy} p_{O_2}$ $\ln\frac{k_4}{k_0} = -\frac{27{,}900}{RT} + 19.23$
	5. $C_4H_2O_3 + 3O_2 \longrightarrow 4CO_2 + H_2O$	$r_5 = k_5 p_{ma} p_{O_2}$ $\ln\frac{k_5}{k_0} = -\frac{30{,}400}{RT} + 20.47$

1. Bailie, Richard, Whiting, Wallace, Shaeiwitz, Joseph, Turton, Richard, and Bhattacharyya, Debangsu. Analysis, Synthesis, and Design of Chemical Processes, Fifth Edition (2018). Web.

Objectives

- Optimize o-xylene (100°C and 1.1 bar) reaction in a PBR / FBR
  - Modeled as a shell-and-tube PFR and an isothermal PFR with 10% bypass, respectively
- Attain **99.9 wt%** Phthalic Anhydride and **95.0 wt%** Maleic Anhydride product streams

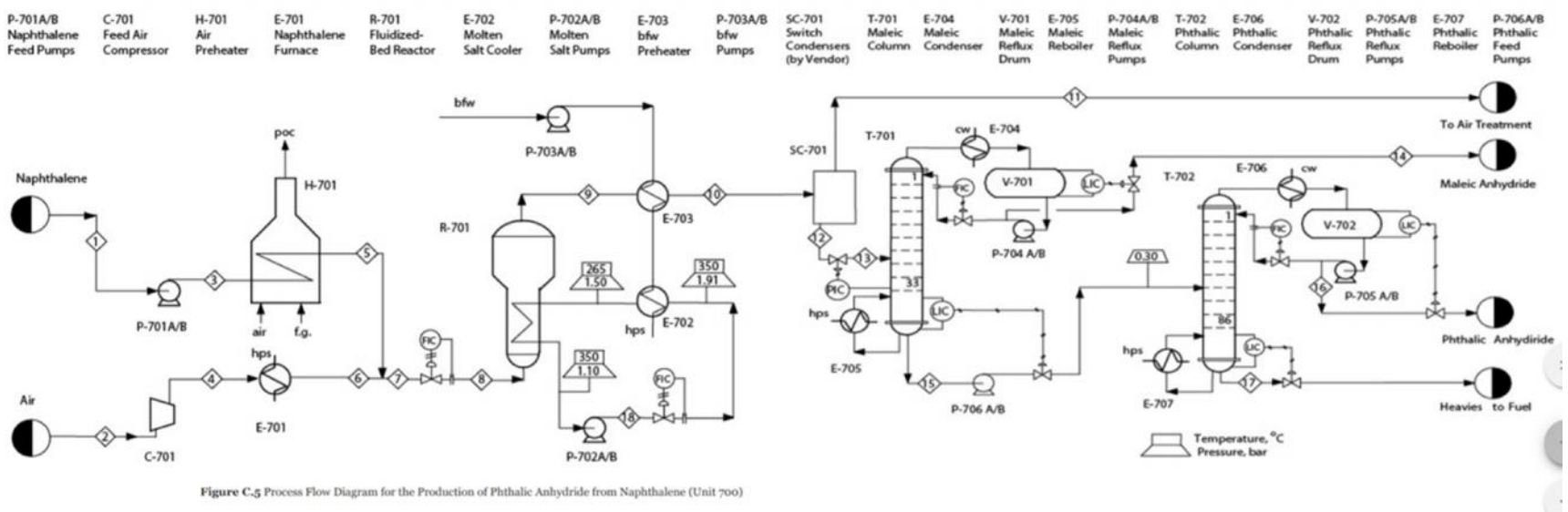


Figure C.5 Process Flow Diagram for the Production of Phthalic Anhydride from Naphthalene (Unit 700)

1. Bailie, Richard, Whiting, Wallace, Shaeiwitz, Joseph, Turton, Richard, and Bhattacharyya, Debangsu. Analysis, Synthesis, and Design of Chemical Processes, Fifth Edition (2018). Web.

Major Hazards and Health Effects of O-xylene

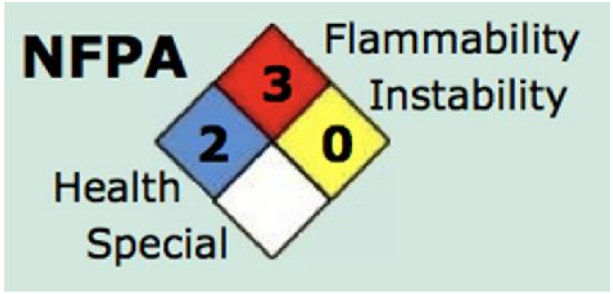
General Description: A colorless watery liquid with a sweet odor. Less dense than water. Insoluble in water[2]

Reactive Group(s): Hydrocarbons, aromatic

Reactivity Alert(s): Highly Flammable

Health Hazards:[3]

- Vapors cause headache and dizziness
- Liquid irritates eyes and skin
- Inhalation: severe coughing, distress, and rapidly developing pulmonary edema
- Ingested: nausea, vomiting, cramps, headache, coma; can be fatal
- Kidney and liver damage can occur



Reactivity Profile:

- Exothermic reaction with oxygen at ambient temperatures
- Intense, violent, or explosive reaction

2. https://www.aiche.org/ccps/resources/chemical-reactivity-worksheet-40
3. https://onlinelibrary.wiley.com/doi/full/10.1002/prs.11833

Major Hazards and Health Effects of Phthalic Anhydride

General Description: Colorless to white lustrous solid needles with a mild distinctive odor. Melting point 64°F Flash point 305°F. Used in the manufacture of materials such as artificial resins.[2]

Reactive Group(s): Anhydrides

Health Hazards:[3]

- Solid irritates skin and eyes; coughing and sneezing
- Liquid: severe thermal burns

Reactivity Profile:

- Reacts exothermically with water
- Incompatible with acids, strong oxidizing agents, alcohols, amines, and bases
- Exothermic nitration with fuming nitric acid-sulfuric acid
- Mixtures of phthalic anhydride and anhydrous CO_2 explode violently if heated

2. https://www.aiche.org/ccps/resources/chemical-reactivity-worksheet-40
3. https://onlinelibrary.wiley.com/doi/full/10.1002/prs.11833

Major Hazards and Health Effects of Maleic Anhydride

General Description: Colorless crystalline needles. Melts at 113°F. Flash point 218°F. Autoignition temperature 890°F.[2]

Reactive Group(s): Anhydrides; Hydrocarbons, Aliphatic Unsaturated

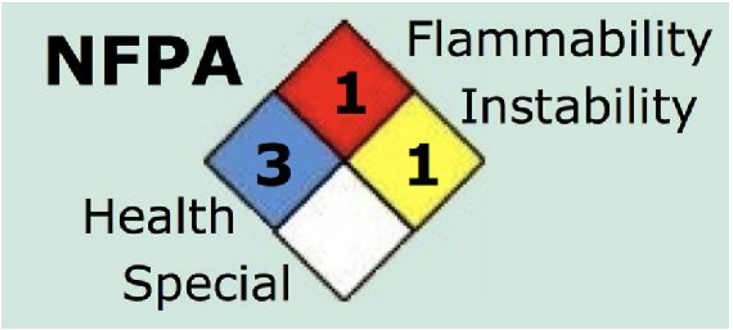
Reactivity Alert(s): Known Catalytic Activity; Water-Reactive

Health Hazards:[3]

- Inhalation: coughing, sneezing, throat irritation.
- Skin contact: irritation and redness
- Vapors:severe eye irritation; photophobia and double vision

Reactivity Profile:

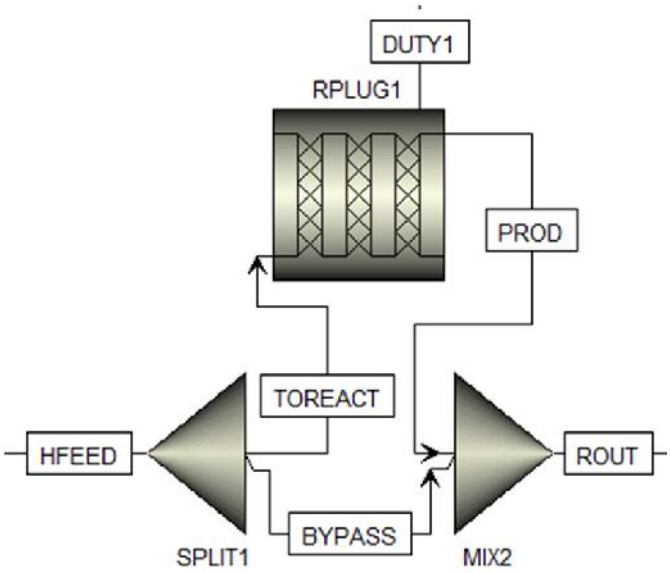
- Reacts vigorously on contact with oxidizing materials
- Exothermic reaction with water or steam
- Undergoes violent exothermic decomposition reactions, producing carbon dioxide



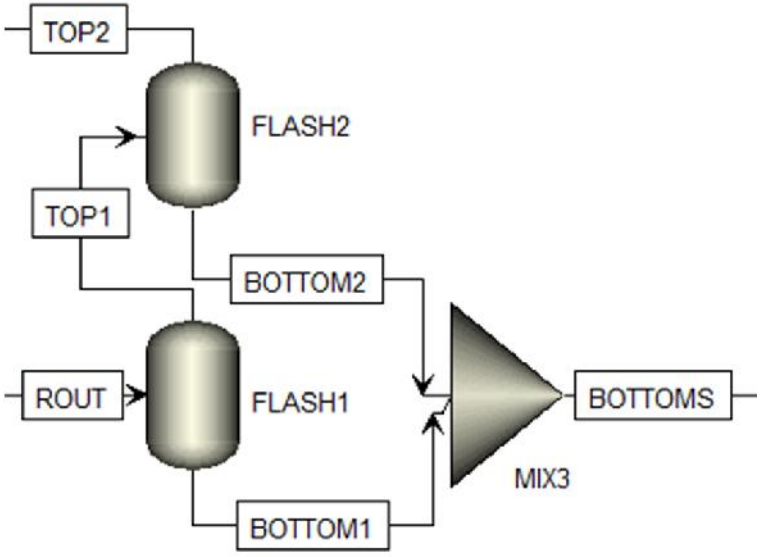
2. https://www.aiche.org/ccps/resources/chemical-reactivity-worksheet-40
3. https://onlinelibrary.wiley.com/doi/full/10.1002/prs.11833

Aspen Plus Simulation Design Choices

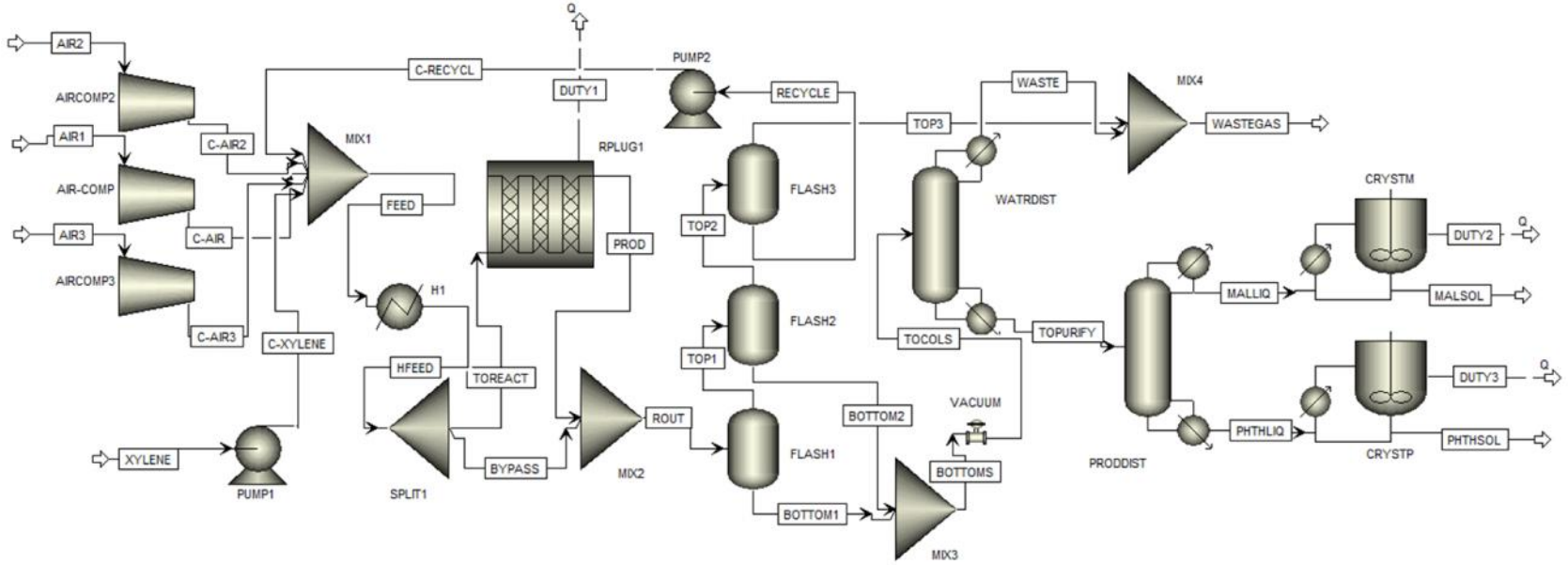
Fluidized Bed Reactor



Switch Condenser Simplification



Aspen Plus Simulation Results



Process Flow Diagram

- **105,558 tonnes** of phthalic anhydride and **1,690 tonnes** of maleic anhydride per year.
- Products are at room temperature and atmospheric pressure.

Aspen Plus Simulation Results

Purity of Products:

	Units	AIR	XYLENE	WASTEGAS	MALSOL	PHTHSOL
+ Mass Flows	**ktonne/year**	**2507.19**	**93.0663**	**2493.01**	**1.69013**	**105.558**
− Mass Fractions						
O-XYL-01		0	1	0.0059468	0.0104126	1.08482e-23
PHTHA-01		0	0	6.14659e-08	0.0388121	0
MALEI-01		0	0	5.96216e-06	0	3.02093e-05
WATER		0	0	0.0161961	2.70916e-09	1.71051e-41
CO2		0	0	0.00217744	0	0
O2		0.243672	0	0.215043	0	0
N2		0.756328	0	0.760631	0	0
PHTH-SOL		0	0	0	0	0.99997
MALE-SOL		0	0	0	0.950775	0

Aspen Plus Simulation Design Choices

- SRK Thermodynamic Model Stream with STEAMNBS free water method
- Recycle stream to reduce raw material waste

Fluidized Bed Reactor	**Packed Bed Reactor (Shell-and-Tube)**
● Uniform temperature profile ● Higher output per unit of investment ● Higher product purity can be obtained ● Efficient heat of reaction recovery	● Tube diameters must be small to avoid hot spots and catalyst damage ● Charging and replacing catalyst is tedious ● Heat recovery from packed bed reactors is difficult

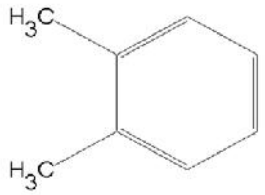
	RECYCLE
− Mass Fractions	
O-XYL-01	0.931117
PHTHA-01	0.00507996
MALEI-01	0.0206108
WATER	0.0425767
CO2	2.01831e-05
O2	0.000238033
N2	0.000357198

4. *Wang, Jyue-Sheng, et al. *Oxidation of ortho-xylene to phthalic anhydride using a fluidized bed catalysis*, 1965.

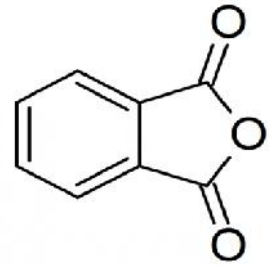
Economic Evaluation

- Total Project Capital Cost: **$44,519,700**
- Revenue: **$65,461,300 in 10 yrs**

- Variable Costs of Production
  - Raw Materials (O-xylene and Air): **$118,905,000 / yr**
    - O-xylene: **$1.40 / kg**
  - Utilities: **$171,802 / yr**



- Fixed Costs of Production
  - Total Operating Cost: **$131,227,000 / yr**
  - Plant Overhead Cost: **$720,000 / yr**
  - Operating Labor Cost: **$1,080,000 / yr**
  - Maintenance Cost: **$360,000 / yr**

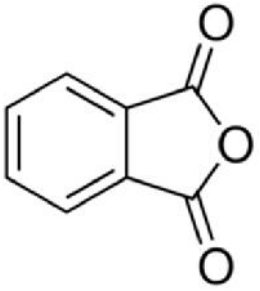


5. "C6: The Price of Para and Ortho Xylene." *Duncan Seddon & Associates Pty. Ltd.*, 2013, http://www.duncanseddon.com/docs/pdf/c6-the-price-of-para-and-ortho-xylene.pdf

Economic Evaluation

- Total Product Sales: **$153,713,000 / yr**
  - Phthalic Anhydride: **$1.61 / kg**
  - Maleic Anhydride: **$1.42 / kg**

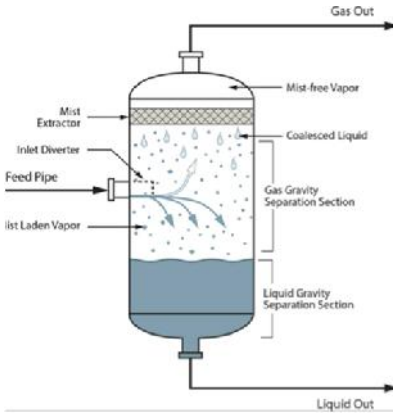
- Economic Evaluation
  - Economic life of project: 10 yrs
  - Payout Period: 9.55 yrs
  - Internal Rate of Return: 21.48%
  - NPV at 10 years: **$4,727,550**
  - Country basis: US

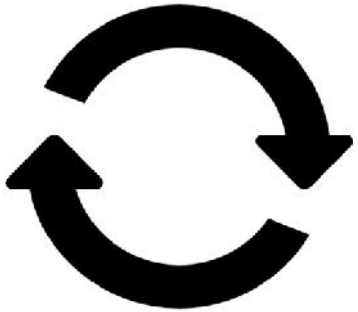


6. “Phthalic Anhydride Price History & Forecast.” *Intratec Solutions*, Intratec Solutions, LLC, 2017, https://www.intratec.us/chemical-markets/maleic-anhydride-price
7. “Maleic Anhydride Price History & Forecast.” *Intratec Solutions*, Intratec Solutions, LLC, 2017, https://www.intratec.us/chemical-markets/maleic-anhydride-price

Conclusions

- Increase plant profitability with a more optimal catalyst
- Additional Flash Separator, Recycle Stream, and Crystallizer





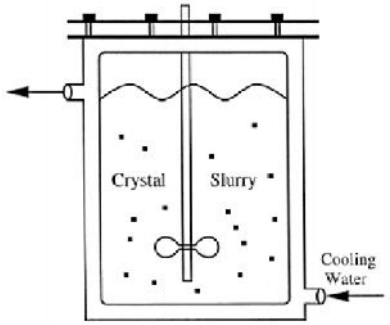


Figure 1. A batch crystallizer

Questions?