

DESIGN OF A FLEXIBLE PROCESS FOR THE PRODUCTION OF n-BUTYL ACETATE AND ISOPROPYL ACETATE

1. Background

Esters are widespread in nature and are responsible for the aroma of many fruits including apples, pears, bananas, pineapples and strawberries. This characteristic has led to extensive use of esters in the fragrance and flavor industries. Furthermore, ester bonds are also found in many polymers and several million tons of polyesters are produced industrially every year. This project involves the production of two different esters: A) n-Butyl Acetate (BuAc) - a chemical used as a solvent for various chemicals including inks, paints, and lacquers; and B) iso-Propyl Acetate (IPAc) – a solvent for cellulose, plastics, oil and fats, and a ingredient in some printing inks and perfumes.

2. Design Objectives

In this project, you will utilize your process design knowledge to develop candidate process flowsheets from the initial concept through material balances, equipment sizing, control system design, and economic analysis. The processes should include all equipment needed to produce the products. A given process may include (but is not limited to) reactors, columns, heat exchangers, extractors, decanters, reflux pots, pumps, storage tanks.

The primary objective of this project is to design a grass-roots facility capable of producing a total of **10,000 metric tons per year** of 99.5 wt% Butyl Acetate. Due to similarities in the reaction schemes and to provide the ability to adapt to changes in market demand, a secondary objective is to evaluate the retrofiting requirements (if any) for switching the Butyl Acetate facility to produce 99.5 wt% iso-Propyl Acetate instead.

You can pursue the design of the BuAc and IPAc processes sequentially, i.e. design the BuAc plant first and then design the IPAc facility using the existing equipment sizes as a starting point to evaluate which pieces of equipment would need to be redesigned, removed or added to the system. Alternatively, you can design the two processes in parallel, i.e. design each plant individually and then evaluate which pieces of equipment could be successfully employed in both processes. It should be emphasized that the **primary objective** is to design the BuAc plant, while the evaluation of the IPAc process is a secondary goal.

For each separation, an analysis of tradeoffs between equipment size and energy or solvent feed (i.e. stages vs. reflux ratio for a distillation column, solvent feed vs. stages for extractors and absorbers, etc.) should be done. For each the minimum number of stages and the minimum amount of flow/energy should be determined to guide your decision regarding the number of trays used in your design. Additionally, the level of an impurity in a stream (e.g. butyl acetate in a butanol recycle stream) should be considered.

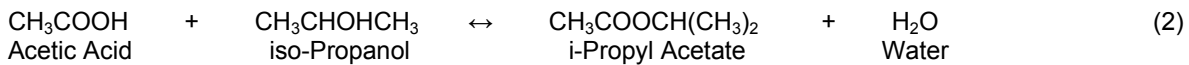
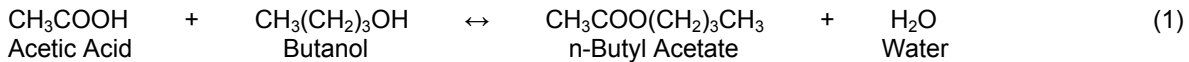
Your final designs must address and adhere to the following specific objectives:

- I. Safety/Environmental Considerations: Your designs must not pose any environmental, health or safety hazards that should have been mitigated with better equipment, instrumentation or control. The processes will generate an ester product stream (BuAc or IPAc) and waste water. In addition, different flowsheets may have additional waste streams. If additional waste streams are generated, the final disposition of those streams must be taken into account both in the process design and in the economic analysis. Additionally, no continuous flaring or venting of hydrocarbons is permitted in the design. This system uses raw materials that are hazardous and/or flammable. Describe your safety concept for the processes. What are the process risks and how can those risks be mitigated? How will you set design pressures and temperatures for your process equipment? Can the principles of inherently safe process design be used to reduce the hazards of this process?
- II. Realistic and Adequate Process Control: Control valves, instrumentation, analyzers, etc. on required equipment to provide safety and minimize personnel danger. It is not necessary to specify each component in detail; a description of what they are and where in the process they are required should be sufficient. It is important to determine not only if your processes are feasible ways of manufacturing the desired esters, but also whether or not they are controllable. You will need to propose a control strategy for the flowsheets. What variables will you control? What variables will

you choose as fixed setpoints? What measured values will your strategy require? Describe how control fluctuations in the reactor may affect the separation. Are there any special requirements for unsteady state conditions, such as start-up or shut-down? Is any additional equipment required to achieve good control, such as hold-up tanks, or heat exchangers? How do your equipment choices affect your control strategy?

3. Reaction and Kinetic Information

Butyl Acetate (BuAc) can be manufactured by the esterification of Acetic Acid (HAc) with Butanol (BuOH) as shown in equation (1) below. Analogously, iso-Propyl Acetate (IPAc) can be manufactured by the esterification of Acetic Acid (HAc) with iso-Propanol (IPOH) as shown in equation (2):



These reactions, like most esterification reactions, are equilibrium limited ($K_{EQ,1} = 10.9 @ 90^\circ\text{C}$ and $K_{EQ,2} = 8.7 @ 90^\circ\text{C}$). This will be **one of the most significant challenges** to design around in this project. The reactions can be catalyzed by any heterogeneous or homogeneous strong acid. The kinetics for the forward and reverse reactions, based on *Amberlyst 15*, a strongly acidic cation exchange resin (equivalent in acidity to 35 wt% aqueous sulfuric acid), are shown in equations (3) and (4) below. The reactor conditions, approach to equilibrium, and sizes can be determined using these kinetics. It can be assumed that these kinetics can also be used to model the esterification of isobutanol and n-propanol with acetic acid to form isobutyl acetate and propyl acetate, respectively.

Pseudohomogeneous model for BuAc on Amberlyst 15:

$$r = m_{cat} (k_{forward} x_{HAc} x_{BuOH} - k_{reverse} x_{BuAc} x_{H_2O}) \quad (3)$$

$$\left[\begin{array}{l} k_{forward} = 3.3856 \cdot 10^6 \cdot \exp\left(\frac{-70660 \frac{\text{J}}{\text{mol}}}{RT}\right) \frac{\text{kmol}}{\text{kg}_{cat} \cdot \text{s}} \\ k_{reverse} = 1.0135 \cdot 10^6 \cdot \exp\left(\frac{-74241.7 \frac{\text{J}}{\text{mol}}}{RT}\right) \frac{\text{kmol}}{\text{kg}_{cat} \cdot \text{s}} \end{array} \right]$$

Langmuir-Hinshelwood model for IPAc on Amberlyst 15:

$$r = m_{cat} \frac{k_{forward} \left(x_{HAc} x_{IPOH} - \frac{x_{IPAc} x_{H_2O}}{K_{EQ,2}} \right)}{\left(1 + K_{HAc} x_{HAc} + K_{IPOH} x_{IPOH} + K_{IPAc} x_{IPAc} + K_{H_2O} x_{H_2O} \right)^2} \quad (4)$$

$$\left[\begin{array}{l} k_{forward} = 7.667 \cdot 10^{-5} \cdot \exp\left(23.81 - \frac{68620.43 \frac{\text{J}}{\text{mol}}}{RT}\right) \frac{\text{kmol}}{\text{kg}_{cat} \cdot \text{s}} \\ K_{EQ,2} = 8.7; \quad K_{HAc} = 0.1976; \quad K_{IPOH} = 0.2396; \quad K_{IPAc} = 0.147; \quad K_{H_2O} = 0.5079 \end{array} \right]$$

In the kinetic expressions above, m_{cat} is the mass of catalyst in kg. You may choose to use a different catalyst for this system. If you do utilize a different catalyst, the impact on the rate must be estimated and the assumptions and methodology utilized should be documented. Additionally, the reasons for choosing a different catalyst must be justified from an economic, product quality, environmental, and/or safety perspective.

4. Physical Properties

The separation of unreacted raw materials and water from the products is complicated by the presence of several azeotropes and other liquid phase non-idealities. While the presence of the associated separation boundaries constitute a challenge, careful consideration of the phase behavior can provide insights that may help in the design of the separation systems. It will be helpful to generate a list of azeotropes in the system as well as any useful thermodynamic features (LLE, SLE, pressure dependence of azeotropes) to develop some initial flowsheets before you begin modeling the process. This can be achieved by using Aspen and/or literature sources. In Tables 1 and 2, azeotropic data is provided for the primary species involved in the Butyl Acetate and Isopropyl Acetate processes, respectively. Furthermore, phase diagrams for both systems are provided in Figures 1 and 2 below.

Table 1: Azeotropes for the BuAc, HAc, BuOH and H₂O system.

Azeotrope	Composition	Boiling Point (°C)
BuOH / BuAc / H ₂ O	(0.0865, 0.206, 0.7075)	90.68
BuAc / H ₂ O	(0.2823, 0.7177)	90.96
BuOH / H ₂ O	(0.2451, 0.7549)	92.62
BuOH / BuAc	(0.7847, 0.2153)	116.85
HAc / BuOH / BuAc	(0.4181, 0.2396, 0.3423)	121.58
HAc / BuOH	(0.5359, 0.4641)	123.21

Table 2: Azeotropes for the IPAc, HAc, IPOH and H₂O system.

Azeotrope	Composition	Boiling Point (°C)
IPOH / IPAc / H ₂ O	(0.2377, 0.4092, 0.3531)	74.22
IPAc / H ₂ O	(0.5981, 0.4019)	76.57
IPOH / IPAc	(0.5984, 0.4016)	78.54
IPOH / H ₂ O	(0.6691, 0.3309)	80.06

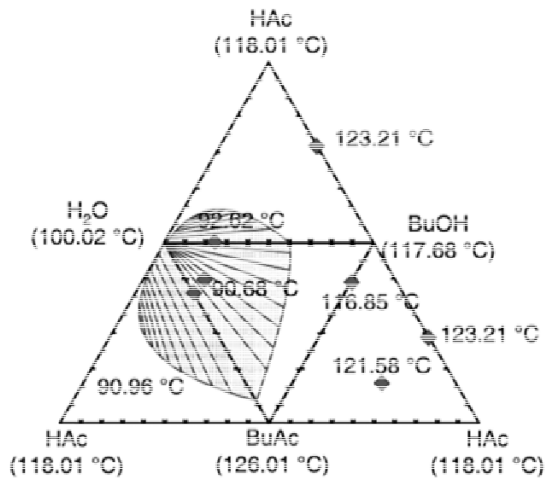


Figure 1: Phase diagram for BuAc, HAc, BuOH, H₂O system.

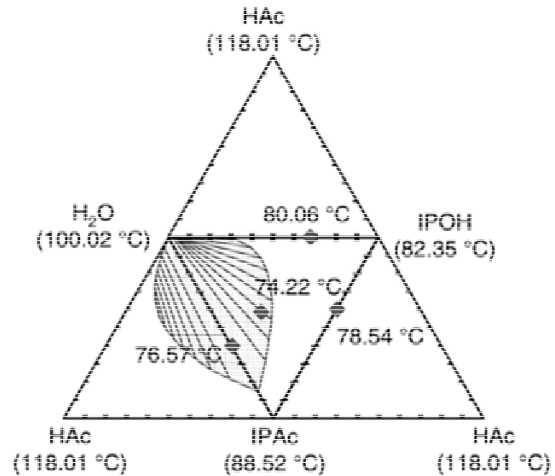


Figure 2: Phase diagram for IPAc, HAc, IPOH, H₂O system.

The choice of thermodynamic property model in Aspen will be critical for obtaining a feasible design. The liquid phase activity coefficient parameters using the UNIQUAC method for BuAc (Table 3) and the NRTL method for IPAc (Table 4) can be used to determine the separation sequence and unit operation sizes and conditions. The coefficients can be judged accurate enough for both vapor/liquid equilibria (VLE) and liquid-liquid equilibria (LLE) calculations. In Figure 3 a screenshot is provided to illustrate how to implement the model parameters in Aspen Plus (shown for BuAc system only).

Additional coefficients for other binary pairs, i.e. isobutanol/water, isobutylacetate/water, n-propanol/water, propylacetate/water etc. must also be determined either from literature values or estimation.

Table 3: UNIQUAC parameters for BuAc system.

Comp. <i>i</i> Comp. <i>j</i>	HAc BuOH	HAc BuAc	HAc H ₂ O	BuOH BuAc	BuOH H ₂ O	BuAc H ₂ O
b_{ij} (K)	66.315	150.193	172.92	-41.53679	-34.227	-345.098
b_{ji} (K)	-74.62672	-358.447	-265.6904	-12.4	-292.4746	-232.247

Table 4: NRTL parameters for IPAc system.

Comp. <i>i</i> Comp. <i>j</i>	HAc IPOH	HAc IPAc	HAc H ₂ O	IPOH IPAc	IPOH H ₂ O	IPAc H ₂ O
b_{ij} (K)	-141.64479	70.96532461	-110.5806744	191.0869653	20.05742325	415.478762
b_{ji} (K)	40.96255662	77.9005536	424.0603422	157.1039255	833.0422748	1373.462808
c_{ij}	0.3048	0.3014	0.2997	0.3000	0.3255	0.3000

The screenshot shows the 'UNIQUAC-1' parameter definition window. The left sidebar lists various property methods, with 'UNIQUAC-1' selected under 'Parameters'. The main window displays a table of temperature-dependent binary parameters. The table has columns for Component i and Component j, and rows for parameters like AIJ, BIJ, CJI, etc. The values are entered in the table cells.

Component i Component j	HAc BUOH	HAc BUAC	HAc WATER	BUOH BUAC	BUOH WATER	BUAC WATER
Temperature units	F	F	F	F	F	F
Source	USER	USER	USER	USER	USER	USER
Property units:						
AIJ	0.0	0.0	0.0	0.0	0.0	0.0
AJI	0.0	0.0	0.0	0.0	0.0	0.0
BIJ	66.315	150.193	172.92	-41.53679	-34.227	-345.098
BJI	-74.62672	-358.447	-265.6904	12.4	-292.4746	-232.247
CJI	0.0	0.0	0.0	0.0	0.0	0.0
CJI	0.0	0.0	0.0	0.0	0.0	0.0
DJI	0.0	0.0	0.0	0.0	0.0	0.0
DJI	0.0	0.0	0.0	0.0	0.0	0.0
TLOWER	0.0	0.0	0.0	0.0	0.0	0.0
TUPPER	1000.000	1000.000	1000.000	1000.000	1000.000	1000.000
EIJ	0.0	0.0	0.0	0.0	0.0	0.0
EJI	0.0	0.0	0.0	0.0	0.0	0.0

Figure 3: Example thermodynamic parameter definition for some binary pairs in BuAc system

Acetic acid and other carboxylic acids exhibit a unique behavior in the vapor phase, even at low pressures. Two or more acetic acid molecules in the vapor phase will associate together (sometimes referred to as vapor phase dimerization) by forming weak bonds between the acidic hydrogen of one acid with the slightly negatively charged, double bonded oxygen of another molecule. This has a significant effect on the vapor phase fugacity coefficient, vapor phase density, and average molecular weight of the acid in the vapor. Fortunately, several equations of state (EOS) have been developed to handle this behavior. In this project it is recommended to use the **Hayden-O'Connell EOS** for the vapor phase if you plan to operate your process under vacuum or at low pressures. If you design your process to operate at higher pressure you will need to consider other vapor phase nonidealities.

5. Reporting Requirements

The project will incorporate a wide range of aspects related to chemical process and product design, e.g. flowsheet synthesis and simulation, heat and mass integration for resource conservation, process optimization, process economics, and also environmental, health and safety related issues. In the following some information is given about the progress reports that need to be submitted during the course of this design project. It must be emphasized that the items listed below are suggested main topics for the content of the reports, they are **NOT** meant as a complete check list. This is an open-ended design project so the project may go in many directions, which are not listed.

5.1. PROGRESS REPORT NO. 1 – THURSDAY FEBRUARY 2, 2012

- Review literature on production, market and economics of acetic acid, butanol, butylacetate, isopropanol and isopropylacetate
- Describe governing chemical/physical principles in each process including phase behavior
- Identify the principal process units necessary to achieve the desired products
- Prepare process flow diagrams for the butylacetate and isopropylacetate processes
- Prepare detailed material balances based on flowsheets
- Prepare preliminary energy balances for flowsheets
- Prepare economic analyses based on the preliminary flowsheets and mass/energy balances

5.2. PROGRESS REPORT NO. 2 – THURSDAY MARCH 8, 2012

- Use ASPEN Plus to develop improved process flowsheet(s) with refined material and energy balances and simulate the primary process equipment
- Perform preliminary economic analyses of the base case design(s)
- Identify and discuss recycle potentials and evaluate the effects on the process economics
- Identify supply and target temperatures for the process streams and perform thermal pinch analyses to identify the potential for heat recovery and reduction in utility usage

5.3. PROGRESS REPORT NO. 3 – THURSDAY APRIL 5, 2012

- Implement material and energy recovery strategies and optimize the design(s)
- Complete the control strategy and include on process flow diagram(s)
- Propose safety concept(s) including inherently safe design considerations
- Complete the energy assessment(s), including thermal pinch analyses
- Review literature for separation and process improvement techniques that can be used to further improve the overall process performance

5.4. FINAL REPORT – FRIDAY APRIL 20, 2012

- Complete the economic analyses including all process options
- Report results from individual team assignment
- Combine the results from all progress reports into one coherent and comprehensive report

6. Individual Team Assignments – March 5-9, 2012

Each team will be assigned one of the following open-ended problems to investigate. These problems will be assigned the second week of March and must be reported in the final report as well as the oral presentation. Some example projects are given below:

- Consider the need for co-locating a new butanol plant. What factors must be considered to choose between the various process technologies available. Are there any synergies associated with co-locating these two processes? What impact will this have on the Net Present Value of the project?
- Consider the need for co-locating a new acetic acid plant. What factors must be considered to choose between the various process technologies available. Are there any synergies associated with co-locating these two processes? What impact will this have on the NPV of the project?
- Consider the need for co-locating a new isopropanol plant. What factors must be considered to choose between the various process technologies available. Are there any synergies associated with co-locating these two processes? What impact will this have on the NPV of the project?

- Evaluate the impact of utilizing acetic anhydride as a raw material instead of acetic acid. What impact will this have on the reactor and separation system design? Acetic anhydride has a higher cost than acetic acid. What is the maximum amount of additional cost per pound of acetic anhydride that can be utilized to still have a cost advantage over using acetic acid?
- Consider in detail the choice of property method in the Aspen Plus simulation. Compare the results using at least three different property methods and determine the impact on the estimated project cost. Quantify the economic risk based on uncertainty in the property method and include this contingency in your final economic assessment. Determine other sources of project risk and attempt to quantify them in your final estimate.
- Process intensification can provide significant benefits in terms of increased efficiency and overall conversion rates. Consider whether combined reaction-separation operations like reactive distillation could be utilized in this process. How should the system be augmented to combine these unit operations? What effect will it have on the control system?

7. Oral Presentation – Last Week of Classes, April 26-27, 2012

The oral presentations of the proposed designs are tentatively scheduled for the last week of classes, i.e. April 26-27, however depending on availability of the external reviewers it may be rescheduled. More information will follow later.

8. Background Literature

The references listed here do not represent a complete list. They serve as a basis for obtaining further information through quoted papers and reports. Furthermore the teams are **strongly** encouraged to use novel sources of information such as the library and World Wide Web.

General Process Description

- Kirk-Othmer Encyclopedia of Chemical Technology
- Ullmann's Encyclopedia of Industrial Chemistry

General Process Design

- Biegler, Grossmann and Westerberg, Systematic Methods of Chemical Process Design
- Douglas, Conceptual Design of Chemical Processes
- Seider, Seader and Lewin, Process and Product Design Principles

Process Economics

- Coulson and Richardson, Chemical Engineering Design – by R.K. Sinnott
- Peters, Timmerhaus and West, Plant Design and Economics for Chemical Engineers

9. A Few Words of Wisdom

- Remember that this is an open-ended project, i.e. you can take the project in almost any direction you find interesting. However you will need to state your reasons for focusing on a specific part.
- During the different stages of the project it will become necessary to make assumptions in order to solve the problems. ALWAYS state your assumptions and the reasons for making them.
- There are many aspects of this project that can be worked on simultaneously. Use your time and efforts wisely so you do not waste valuable time waiting for help on just one part of the project.
- The instructor is there to help you, so use him.

APPENDIX

A.1. General Information

- Standard conditions are 60°F and 14.7 psia.
- Short ton = 2000 lb

A.2. Raw Material and Product Cost Information

All the cost information provided here can be used as the basis for the design, however you are encouraged to look up updated prices throughout the semester to evaluate the stability of the markets. The products are to be transported to existing storage tanks and then loaded onto vessels for transport.

- Acetic acid feed (99.85 wt% HAc, 0.15 wt% H₂O): \$0.36/lb
- Butanol feed (99.80% BuOH, 0.10 wt% H₂O, 0.10 wt% i-BuOH) \$0.65/lb
- Isopropanol feed (99.80% IPOH, 0.10 wt% H₂O, 0.10 wt% n-PrOH) \$0.55/lb
- n-Butyl acetate (99.5 wt% BuAc, max. 0.25 wt% alcohols, max. 0.1 wt% H₂O) \$0.95/lb
- i-Propyl acetate (99.5 wt% IPAc, max. 0.25 wt% alcohols, max. 0.1 wt% H₂O) \$0.90/lb
- Amberlyst 15 (must be replaced every 2 years to maintain maximum activity) \$45.00/lb

A.3. Utility Cost

Steady-state design may not require all utilities. You can ignore transient start-up requirements for this preliminary design in terms of utilities. You have several utilities available to you both for heating and cooling. These utility levels have different costs associated with them as shown below. You will need to determine what conditions you will run your unit operations based on these utilities. You should also consider what the economic impact (both capital and operating cost) would be of heat integration.

Table 5: Utility cost.

Utility	Cost	Credit
HP Steam (600 psig steam, 490°F)	\$5.00/1000 lb consumed	\$4.00/1000 lb produced
MP Steam (125 psig steam, 353°F)	\$4.00/1000 lb consumed	\$3.00/1000 lb produced
LP Steam (20 psig steam, 260°F)	\$3.50/1000 lb consumed	\$2.50/1000 lb produced
Electricity	\$0.04/kWh consumed	\$0.03/kWh produced
Fuel Gas	\$3.00/million BTU consumed	\$2.00/million BTU produced
Steam Condensate (>99.9% v/v pure)		\$2.00/1000 lb produced
Process Water (>99% v/v pure)	\$0.50/1000 gal consumed	\$0.35/1000 gal produced
Cooling Water (supply 25°C, return 35°C)	\$0.40/1000 gal consumed	\$0.30/1000 gal produced
Brine Refrigeration (supply -5°C, return 5°C)	\$4.00/ton	
Waste Water Treatment (>95% v/v pure)	\$6.00/1000 gal produced	