Group Project #1: Process Flowsheeting Calculations for Acetic Anhydride Plant

Date: 2/25/00
Due: 3/3/00

ⓒPaul I. Barton, 14th February 2000

At our Nowhere City facility we purchase acetic anhydride as a feed for our Fixit unit. We also make both glacial acetic acid and acetone, from which acetic anhydride can be manufactured. Recent production and sales trends lead us to consider making acetic anhydride in house, rather than purchasing it. This can be accomplished by cracking the acetone to ketene and then reacting the ketene with acetic acid to produce the acetic anhydride.
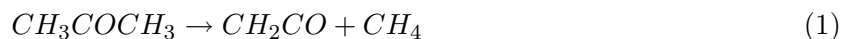
A preliminary evaluation of the feasibility of manufacturing acetic anhydride versus purchasing it has recently been completed. The results of this study, and the flowsheet structure synthesized are described in this document (see figure 1).

Following this study, management has requested the development of a detailed flowsheet model of the proposed process using ASPEN PLUS. Will you please develop this model and solve the steady-state material and energy balances for the base case operating parameters (as outlined in this document).

Management requires the results of your calculations on 3rd March. I expect a full report that includes a process flow diagram, stream tables, and details of your calculations and assumptions by 10am that day.

Process Chemistry

The unfamiliar chemical species in this process are: acetone (dimethyl ketone) (CH_3COCH_3), ketene (CH_2CO), acetic acid (CH_3COOH), and acetic anhydride ($(CH_3CO)_2O$). The acetone cracking reaction is:
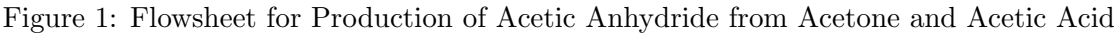
$$CH_3COCH_3 \rightarrow CH_2CO + CH_4 \tag{1}$$

The ketene decomposition reaction is:

$$CH_2CO \rightarrow CO + \frac{1}{2}C_2H_4 \tag{2}$$

The acetic anhydride formation reaction is:

$$CH_2CO + CH_3COOH \rightarrow (CH_3CO)_2O \tag{3}$$

Some pure component parameters for the species present in the process are shown in Table 1.

Figure 1: Flowsheet for Production of Acetic Anhydride from Acetone and Acetic Acid

Species	MW (gmol)	Normal BP (K)	T^c (K)	P^c (bar)
Acetone	58.08	329.24	508.1	47.01
Acetic Acid	60.05	391.1	594.4	57.86
Acetic Anhydride	102.09	412.0	569.0	46.81
Ketene	42.04	232.0	380.0	64.85
Carbon Monoxide	28.01	81.7	132.9	34.96
Methane	16.04	111.7	190.6	46.00
Ethene	28.05	169.4	282.4	50.36

Table 1: Pure Component Parameters for the Acetic Anhydride Process

Process Description

The preliminary design team has proposed the flowsheet shown in figure 1. The process operates at or near atmospheric pressure throughout. You are free to alter this flowsheet structure. Your flowsheet should produce 50,000 (short) tons per year of acetic anhydride, assuming an operating time of 8,150 hours per year.

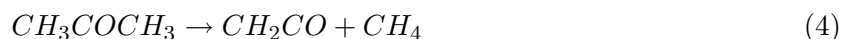### Feed Streams and Utilities

The process has the following feed streams and utilities:

1. acetone is available as a liquid at 1 atm and 30°C, effectively pure.

2. acetic acid is available as a liquid at 1 atm and 30°C, effectively pure.

3. cooling water is supplied at 30°C with a maximum return temperature of 40°C.

4. steam is available at five pressure levels: 212F, 268F, 366F, 448F and 514F.

5. fuel gas and electricity are available are required.

Assume heat exchangers have a minimum temperature difference of 10°C between streams exchanging energy.

Acetone Cracking Furnace

Fresh liquid acetone is mixed with liquid acetone recycled from the acetone column and fed to the cracking furnace. The mixture is first vapourized and then heated to 700°C, where the thermal decomposition of acetone to ketene takes place in the vapour phase according to the reaction:

$$CH_3COCH_3 \rightarrow CH_2CO + CH_4 \tag{4}$$

Ketene is an extremely unstable compound, and at these temperatures any ketene formed by the above reaction will decompose rapidly according to the reaction:

$$CH_2CO \rightarrow CO + \frac{1}{2}C_2H_4 \tag{5}$$

Pilot plant studies indicate that both these reactions are taking place in the cracking furnace. Experimental data from these pilot studies have been regressed to yield the following correlation:

$$y = 1 - 1.25x \tag{6}$$

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where x is conversion of acetone in furnace given by:

$$x = \frac{F_{acetone,in} - F_{acetone,out}}{F_{acetone,in}} \tag{7}$$

and y is the yield of ketene given by:

$$y = \frac{\text{moles of ketene leaving furnace}}{\text{moles of acetone reacted}} \tag{8}$$

This linear correlation fits the data well for acetone conversions less than 0.5. The base case design requires the cracking furnace to be operated at an acetone conversion of 0.15.

Quench Reactor

In order to quench the thermal decomposition of ketene rapidly, hot gases exiting the cracking furnace are first cooled by injecting liquid acetic acid. The resulting gaseous mixture is then fed to the quench reactor where the hot rising gases are contacted with a falling spray composed of acetone, acetic acid and acetic anhydride.

Once the ketene has condensed, acetic anhydride is formed in the quench reactor by the following liquid phase reaction:

$$CH_2CO + CH_3COOH \rightarrow (CH_3CO)_2O \tag{9}$$

Pilot plant studies indicate that the quench reactor should be operated at 80°C, and, in order to drive the reaction to completion, the molar ratio of acetic acid to ketene fed to the quench reactor must be at least 6:1. It can be assumed that the vapour and liquid streams leaving the quench reactor are in phase equilibrium with each other, and all the ketene is consumed by reaction.

Heat is removed from the quench reactor by recycling and cooling a fraction of the liquid stream leaving the reactor. This forms the feed for the spray device. As this recycle stream has a relatively minor effect on the overall mass balance around the reactor, it can be neglected. However, the cooling duty for the quench reactor cannot be neglected.

Acetone Condenser and Flash Drum

The gaseous by-products leaving the quench reactor at 80°C carry with them a significant quantity of acetone. This acetone must be recovered and recycled. As a first step, the gas is cooled to 40°C (the lowest temperature that can be achieved without refrigeration) in a partial condenser, and the resulting two phase mixture is separated in a flash drum.

Acetone Absorber

The vapour leaving the acetone flash drum still has a high acetone content. The vapour is fed to a plate absorption column where it is contacted with a liquid stream composed of predominantly acetic acid. This absorbs most of the remaining acetone from the gaseous by-products. Acetic acid was chosen as a solvent so as not to introduce another chemical species into the system.

Preliminary design calculations indicate that about seven theoretical stages are adequate for this separation. The vapour leaving the absorption column is sent to an aqueous scrubber in order to recover acetic acid (do not include this unit in your calculations) and the resulting dilute solution of acetic acid is fed to the acetic acid concentration plant. In order to recover acetic acid in this manner, the mole fraction of acetone in the vapour stream exiting the acetone absorber must be less than 0.01. The gaseous by-products may be utilized as fuel.

These decisions result in three liquid streams that must be separated by the liquid recovery system: the liquid stream from the quench reactor, the liquid stream from the acetone flash drum, and the liquid stream from the acetone absorber. From the boiling points of the liquid species, distillation has been chosen as the most suitable separation technology for these mixtures.

Acetic Anhydride Column

The liquid stream leaving the quench reactor contains the highest concentration of the product acetic anhydride. Hence, the first column splits pure acetic anhydride product from the other components. The product is withdrawn from the bottom of the column and cooled to 40°C before being pumped to storage. The Fixit unit requires acetic-anhydride of 99.9% purity.

For the base case design, the column was designed to recover 99% of the acetic anhydride fed to the column in the bottoms stream.

Acetone Column

The overhead stream from the acetic anhydride column is mixed with the liquid stream from the acetone flash drum and the liquid stream from the absorber to form the feed to the acetone column. This mixture is predominantly acetone and acetic acid, but also contains acetic anhydride and traces of the gaseous species. The column splits this mixture to produce an overhead stream rich in acetone and a bottoms stream rich in acetic acid. The condensed overhead stream is recycled to the cracking furnace,[1] and the bottoms stream is recycled to form the solvent feed for the absorber and the acetic acid feed for the quench reactor.

For the base case design, the column was designed to recover 99% of the acetic acid fed to the column in the bottoms stream, and 99% of the acetone fed to the column in the overhead stream.

Reporting Requirements

The calculations will be undertaken in groups of three students (allocated by e-mail already). Care should be taken to break the problem into subtasks and thus divide the labour. The report should adhere to the following format:

1. **Summary**: short (less than one page) summary outlining a motivation for the project, calculations undertaken, summary of key results, and an outline of the rest of this report. This summary would be used by senior management to assess the success of your work.

2. **Process Description**: description of the process flowsheet. Detail any changes to flowsheet structure or operating parameters required to make the problem feasible.

3. **Process Flow Diagram and Stream Tables**: give flowrate, composition, pressure, temperature, enthalpy flow, and phase of all streams.

4. **Model Formulation**: discuss any assumptions and/or simplifications introduced in formulation of the process model with a justification. Discuss the physical property models employed, with supporting rationale and data.

5. **Flowsheeting Calculations**: decomposition strategy, initialization and convergence method used, particular problems encountered. Brief mathematical analysis of results, e.g., check overall balances, estimate numerical errors, are design specifications satisfied?

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[1] why condense a stream only to vapourize it again in the furnace? Think about it.

6. **Appendix**: Aspen Plus input file (.inp) and report file (.rep) for your final converged flowsheet.

Use the METCBAR units set throughout.

Problem Decomposition

You are undertaking a complex modeling task within a limited period of time. Your success will hinge on your ability to work as a team and divide the labour. It is vital to build the flowsheet model in an evolutionary manner; the full blown model will not converge first time from default initial guesses. As general guidelines:

- start with a unidirectional flowsheet, and then add in recycle streams one at a time.
- do material balance only calculations, and then material and energy balance calculations (Aspen Plus allows you to switch off energy balance calculations).
- use simple models (e.g., SEP2), and then more rigorous models (e.g., RADFRAC).
- use the results of earlier calculations as initial guesses for more rigorous calculations, and put tight bounds on manipulated variables. You may want to use different flowsheet decompositions for simpler models (e.g., certain features of the flowsheet only effect the energy balance). Use back of the envelope calculations and knowledge of the process to suggest reasonable values for both.
- do simulation and/or sensitivity calculations first and then design calculations.
- use ideal physical property models and then more rigorous/appropriate models later.

It is also worthwhile devoting some time to thinking about how the overall task can be split into a series of subtasks that can be worked on by individuals in parallel. For example, initially the following three tasks can be done in parallel:

1. develop and converge a material balance only model of the flowsheet (simple models).
2. research physical property models and validate with experimental data.

At the end of this phase, you should have good initial guesses ($\pm 10\%$) for the material flows in the flowsheet and a decision concerning a good physical property model. In the second stage:

1. build a material and energy balance model for the flowsheet (Figure 1) using SEP2 blocks for the distillation columns. Then start adding design specifications one by one.
2. with good guesses for the liquid feeds to the distillation columns, get shortcut and then rigorous models working for the distillation columns.

Continue by replacing SEP2 blocks with RADFRAC blocks in the material and energy balance model one at at time, each time using the results of the previous calculations as initial guesses for the next. Finally, add the design specifications one at time.