Our company plans to evaluate the economics for a process to manufacture formaldehyde from methanol. Currently, we buy formaldehyde for manufacturing adhesives and wish to explore whether or not we would be better off manufacturing it for our own use. The consulting company Designs-Are-U's has recommended a process that employs a molybdenum oxide catalyst. The pertinent reactions are listed below.

\[
\begin{align*}
\text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} & \zeta_1 \\
\text{CH}_2\text{O} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} & \zeta_2 \\
\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 & \zeta_3
\end{align*}
\]

The extent of reactions is determined by the processing conditions. A simplified process flow diagram is shown in Figure 1.

**Process Description**

Air fresh feed (Stream 1) is mixed with a recycle stream to form Stream 2. Methanol fresh feed (Stream 3) is vaporized and mixed with Stream 2. The reactor feed (Stream 4) is maintained at a methanol-to-oxygen ratio of $1/3$. This keeps the methanol concentration below its lower explosive limit. The reactor feed in Stream 4 is heated to reactor temperature and passed through the catalyst bed. The feed residence time in the reactor is kept very short to limit conversion to primarily formaldehyde. The reactor conditions may be varied to adjust single-pass conversion. The product gases from the reactor are cooled and sent to an absorber. Deionized water (Stream 7) is pumped into the top of the absorber. The water dissolves essentially all of the formaldehyde and some of the methanol. The absorber temperature controls the amount of formaldehyde and methanol dissolved. The flow of water to the absorber is adjusted so that the product contains 37 wt% formaldehyde and some methanol. The methanol impurity is normal and is acceptable in the range of 0.0 to 2.0 wt%. Stream 8 contains CH$_2$O and CH$_3$OH that are not absorbed, as well as O$_2$, N$_2$, CO, CO$_2$ and H$_2$O. The absorber temperature determines the mole fraction of water vapor in Stream 8. Stream 8 is split into recycle (Stream 10) and purge (Stream 9). The fate of the purge stream will not be considered in this problem. However, it will be sent to a catalytic combustor so that the process will have zero hazardous emissions.

**Reaction Selectivity**

The consulting company has provided data on typical catalyst performance as a function of single-pass methanol conversion. These data are presented in Table 1.
Table 1. Methanol Conversion and Product Yield

<table>
<thead>
<tr>
<th>CH$_3$OH Conv. (%)</th>
<th>85.6</th>
<th>91.5</th>
<th>95.3</th>
<th>98.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Yield CH$_2$O</td>
<td>85.0</td>
<td>90.0</td>
<td>93.0</td>
<td>95.0</td>
</tr>
<tr>
<td>CO</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.1</td>
<td>0.5</td>
<td>0.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Absorber Efficiency

The amount of CH$_2$O and CH$_3$OH absorbed by water in the separator is determined by operating temperature and pressure. These conditions also determine the mole fraction of water in Stream 8. Absorber efficiency data and mole fraction of water vapor in the off gas is provided in Table 2. The water flow to the absorber must be adjusted to produce an aqueous solution of 37 wt% CH$_2$O. This is the standard concentration for formaldehyde solutions and what we currently purchase for our adhesives manufacturing process.

Table 2. Absorber Performance Data

<table>
<thead>
<tr>
<th>Absorber Efficiencies</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$O</td>
<td>99.9</td>
<td>99.85</td>
<td>99.8</td>
<td>99.7</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>80.0</td>
<td>60.0</td>
<td>40.0</td>
<td>20.0</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Mol% H$_2$O in Stream 8 | 4.0 | 6.0 | 8.0 | 10.0

Changing Recycle-to-Purge Ratio

The recycle-to-purge ratio affects the amount of feed that is lost to the purge stream. To test the effect of large changes in recycle-to-purge ratio, you should plan to evaluate this process at the following three ratios:

| Recycle-to-purge ratio | 4/1 | 9/1 | 20/1 |

Operating Costs

Information on operating costs and the cost/value of reactants and products will be provided in a subsequent memo.

Problem

Your design group is asked to calculate the most profitable mode to operate the proposed formaldehyde production unit. The unit should be evaluated on the basis of producing 50,000 tonnes of CH$_2$O per year (1 tonne = 1000 kg). You are to determine what level of conversion, what absorber efficiency and what recycle-to-purge ratio are most profitable.
Since there are 4 conversion levels, 4 absorber efficiencies and 3 recycle ratios, a total of 48 cases need to be evaluated. With so many cases to consider, you will benefit by working with a group and using the computer for calculations.

Group Formation

A design group is to consist of two members. You are encouraged to make groups by yourselves. When you have formed a group, please turn in the names of group members to Dr. Kugler. He will combine groups to make 3- or 4-person design teams. A list of design teams will be provided on November 15.

Computations

You are expected to use a spreadsheet for material balance and cost calculations. The first step should be solving the material balance by hand calculations. Use a basis of $M_4 = 100$ kmol and the first set of conditions for the reactor, absorber and recycle ratio. After completing the hand calculation, set up the spreadsheet to do the material balance when you specify reactor, absorber and recycle conditions. Copy results into a stream table. These first steps, including pencil-written, hand calculations, should be included as an appendix to your report to demonstrate that calculations were done correctly.

After producing a stream table on your spreadsheet using kmol units, convert kmoles to mass on a second stream table, then scale so that formaldehyde meets production goal. Profit or loss should be calculated from scaled-stream-table data.

Reports

Each team will be expected to prepare a written report recommending the best operating procedures for the formaldehyde process. This report is due at 3:00 PM, Wednesday, December 6. The report should follow the department’s design-report guidelines. Data should be in the form of graphs and tables since this serves to both condense results and make them easier to read. The appendix should include your spreadsheet and a hand calculation of the first case.

Report Authors

Although work on a group report can never be divided equally, only those members making substantial contributions to the calculations, spreadsheets or final report should be listed as authors.

E. L. Kugler
November 13, 2006
Supplemental Information
CHE 201 Project

Operating Costs

Designs-Are-Us has contacted several formaldehyde manufacturers about their operating costs and provides the following information.

Base operating cost: $0.020 per pound of methanol feed
Recycle cost: $0.008 per pound of recycle gas in Stream 10

Value of Feeds and Products

Methanol fresh feed $0.28 per pound
Deionized water $0.005 per pound
Air fresh feed $0.00 per pound
Formaldehyde $0.50 per pound
Purge gas $0.00 per pound

Profit (Loss) on Process

At a selling price of $0.50 /lb, the value of 50,000 tonnes of formaldehyde is $55.0 million. In estimating profit or loss for various operating conditions, the significant figure for profit or loss should be 0.1 million.

E. L. Kugler
November 27, 2006
Figure 1: Formalin from Methanol