Suggested Design Projects – 2001-2002

1. Vinyl Chloride from Ethane
   (recommended by John Wismer, Atochem North America)

Vinyl chloride is a major commodity chemical. Worldwide consumption exceeds 50 billion lb/yr. The vast majority of vinyl chloride monomer (VCM) is used in the production of PVC (polyvinyl chloride), which has a broad variety of applications. Vinyl chloride is also the main building block for hydrochlorocarbons and hydrofluorocarbons. Worldwide growth trends are very positive.

Your firm (Penn Consultants) has just been awarded a contract from one of the country’s major producers of VCM. The client is an operating company that has sought to become a low-cost producer by running with minimal overheads (no R&D) using a mature technology. This technology is used almost universally to make VCM. The process combines direct chlorination with oxychlorination of ethylene to make ethylene dichloride (EDC – also, dichloroethane).

\[
\begin{align*}
1) \quad & \text{C}_2\text{H}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 \\
2) \quad & \text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 + 2\text{HCl} \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + \text{H}_2\text{O} \\
3) \quad & 2\text{C}_2\text{H}_4\text{Cl}_2 \rightarrow 2\text{C}_2\text{H}_3\text{Cl} + 2\text{HCl}
\end{align*}
\]

EDC is then converted to VCM in a pyrolysis furnace:

HCl from the furnace is recycled to step 2, allowing the process to stay in balance with respect to HCl. A good summary of the technology, with a basic flowsheet, can be found in the *Encyclopedia of Chemical Technology, Fourth Edition* by Kirk and Othmer.

Your client is planning capacity expansions but is concerned about new technologies being developed by competitors that invest heavily in R&D. For the most part, these technologies use ethane, which is cheaper than ethylene, as a feedstock. In fact, ethane is a major feedstock used in the production of ethylene so an ethane-based process eliminates a processing step. Historically, ethane-based processes have had too low a selectivity to be practical. However, there have been some notable recent improvements (see U.S. Patent 5,763,710). Your client’s immediate concern is with a recent patent application filed in Europe by one of their major competitors, Dow Chemical Company (WO0138274 - May, 2001). This is a detailed 85-page application with block diagrams and examples demonstrating how their relatively selective ethane-based process might work. The major breakthrough claimed by Dow is that they can simultaneously convert ethane and ethylene to EDC. This is significant in that ethane-based routes produce a significant amount of ethylene non-selectively. Dow claims that they can recycle this to the reactor used to convert the ethane.
Your client has asked your firm to evaluate the potential of this technology by designing a plant and evaluating its capital costs and production requirements. Be optimistic because your client wants to know the best possible scenario. At the same time, you need to identify the significant technical hurdles that Dow might face before commercializing this technology. Assume a plant capacity of 1 billion lb/yr of VCM. Since the ethane technology is a net producer of HCl, the economic analysis must account for the HCl by-product. HCl is a chemical commodity with a volatile price history. However, the current supply/demand balance is favorable to producers and optimistic projections would allow a credit $0.07/lb for by-product HCl. Ethane, ethylene, and chlorine are also commodity chemicals. Price histories may be available from a number of sources including the Bureau of Labor Statistics.

In addition to their concern over Dow building grass roots plants with their technology, your client is concerned about whether Dow can retrofit their existing oxychlorination plants to handle this technology. Without doing a detailed analysis of this mature technology, give a qualitative opinion on retrofittability based on the fundamentals of each process.

References:


U.S. Patent 5,763,710

World Patent 01738274, May 2001

2. Fuel Processor for 5 KW PEM Fuel Cell Unit
(recommended by Jianguo Xu and Rakesh Agrawal, Air Products and Chemicals)

Fuel cell technology is considered to be a disruptive energy technology. Fuel cells use fuel in an electrochemical combustion process that converts the chemical potential of the fuel with respect to the combustion product directly into electrical power. They are more efficient and more environmentally friendly than conventional energy technologies. Fuel cells, especially the proton exchange membrane (PEM) fuel cell, are being considered for distributed power generation (DG). Using a fuel cell for DG reduces the energy loss due to power transmission, and can eliminate power outages due to weather-related or other causes. It also allows for efficient use of the low-level waste heat from the power generation process. This low-level heat can be used for producing hot water, and for room heating. Since the PEM fuel cell uses hydrogen gas as fuel, a supply of hydrogen gas has to be installed for a fuel-cell power generator to work.

Hydrogen for use in residential fuel cells can be produced from pipeline natural gas using a fuel processor. Assume that a residential, fuel-cell, electric-power generator with 5 kW electricity output has an efficiency of 50% (the electricity output from the fuel cell is
50% of the lower heating value of the hydrogen consumed in the fuel cell). The desired hydrogen pressure is 0.5 barg. Note that the CO content in the hydrogen supplied to the fuel cell must be below 10 ppm, and the sulfur content must be less than 0.1 ppm. Nitrogen, carbon dioxide, methane, water vapor, and other inert gases are not poisonous to the fuel cell. For design purposes, a fuel gas with less than 3 vol% of hydrogen cannot be used to fuel the fuel cell.

A possible approach: Natural gas can be converted at a high temperature into hydrogen, CO, CO2 (syngas) in a steam reformer or partial-oxidation reactor, or autothermal reformer which is a combination of the first two. Most of the CO in the syngas is typically converted into carbon dioxide at a lower temperature in a water-gas shift reactor. The remaining small amount of CO must be removed to below 10 ppm level. This can be done using adsorption, or membrane separation, or catalytic preferential oxidation (at about 90°C with an air stream), or other practical means. Also, there are designs with membrane reformers in the literature.

Natural gas composition and pressure: use that available at the sight of your plant. If no data can be found, use the data below:

<table>
<thead>
<tr>
<th></th>
<th>vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>95</td>
</tr>
<tr>
<td>ethane</td>
<td>2.0</td>
</tr>
<tr>
<td>propane</td>
<td>1.5</td>
</tr>
<tr>
<td>butane</td>
<td>0.65</td>
</tr>
<tr>
<td>pentane</td>
<td>0.35</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.5</td>
</tr>
<tr>
<td>organic sulfur</td>
<td>2 ppm</td>
</tr>
</tbody>
</table>

5 barg

References:

*Chemical Engineering*, July 2001, pp. 37-41
3. Batch Di (3-pentyl) Malate Process
(recommended by Frank Petrocelli and Andrew Wang, Air Products and Chemicals)

Your company, a small specialty chemicals manufacturing operation, is considering producing di(3-pentyl) malate for the additives market. Your marketing team has projected the following sales estimates for this product:

<table>
<thead>
<tr>
<th>Anticipated Sales (in thousands of pounds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year</td>
</tr>
<tr>
<td>Sales @ $6.50/lb</td>
</tr>
<tr>
<td>Sales @ $8.00/lb</td>
</tr>
</tbody>
</table>

You currently have a fully depreciated, 1,000-gallon batch reactor that is used to manufacture another product (Product X). This reactor is made of 316SS, which is sufficiently corrosion-resistant for producing the new product as well. Product X is made in 6,000-pound batches that require 36 reactor hours per batch and is sold at a profit of $0.88 per pound. 100 such batches are produced annually (not expected to change); the rest of the time the reactor is idle. This reactor is jacketed for heating and uses 175 psig saturated steam. The jacket has a heat-transfer area of 88 ft² and an estimated overall heat-transfer coefficient of 100 Btu/ft²hr°F.

Di(3-pentyl) malate is made by batch reaction of malic acid with an excess of 3-pentanol, using 0.1 weight percent of an acid catalyst such as sulfuric acid (see reaction above). Water is produced as a co-product and must be removed to drive the reaction to completion. Water and 3-pentanol form a low-boiling azeotrope (see CRC Handbook for data) that forms two liquid phases upon condensation. A typical process scheme would be to carry out the batch reaction above the azeotrope temperature while condensing the overhead vapors into a decanter, recycling the organic layer to the reactor and removing the aqueous layer (Figure 1, top). This approach can be used with your existing reactor. A more sophisticated approach would involve interposing a distillation column between the reactor and the condenser, allowing the alcohol-rich vapors off the reactor to strip water out of the organic recycle (Figure 1, bottom). When the desired conversion is achieved, the product must be treated with aqueous sodium hydroxide to neutralize the residual acidity (due both to the catalyst and the unreacted malic acid). The residual 3-pentanol must be stripped off using vacuum (50 mm Hg) with nitrogen sparge at 120°C. Your R&D group has come up with the mass-transfer estimates given in Table 1.
Finally, the product must be filtered to remove the salts of neutralization. Your company currently has no vacuum or filtration equipment.

Table 1. Mass Transfer Data

\[
\frac{dx}{dt} = k_l a (y^* - y)
\]

where \( x \) is the mole fraction of 3-pentanol in the liquid, \( y^* \) is the vapor phase mole fraction of 3-pentanol in equilibrium with \( x \), and \( y \) is the vapor phase mole fraction of 3-pentanol. Assume that the Henry’s law constant for 3-pentanol in the product is 1200 mm Hg.

<table>
<thead>
<tr>
<th>Superficial Gas Velocity (scf/ft²,min)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_La ) (1/hr)</td>
<td>0.076</td>
<td>0.12</td>
<td>0.17</td>
<td>0.24</td>
<td>0.37</td>
</tr>
</tbody>
</table>

The required product specifications are:
- Residual acidity (prior to neutralization) \(< 0.1N\)
- Residual 3-pentanol \(< 0.1 \text{ wt.\%}\)
- Purity (moles ester / total moles) \(> 98 \text{ wt.\%}\)

You are being asked to provide the following:
1. An equipment design for a dedicated batch-reactor system to produce dibutyl malate, including a capital cost estimate for both process options shown in Figure 1.
2. A batch ticket for a typical production batch. This will itemize the individual steps the operator will follow to produce the batch, including amounts of materials being added, estimated duration of each step and the safety procedures and precautions that must be followed. It should also specify when samples must be taken and what the criteria are for proceeding to the next step.
3. A recommendation to management on whether/when to build the dedicated equipment or use the existing reactor, supported by appropriate financial information.

Key process determinations:
- Which process option should you use for a new design – with or without the distillation column?
- How much heat-transfer surface is required and what heating medium (assume you have saturated steam available at 175 psig for $5 per million Btu)?
- What type of agitation is needed (horsepower and impeller design)?
- How long will the reaction take? What is the reaction profile (concentrations and temperature vs. time)? How does the composition of the vapor from the reactor change with time?
- What ratio of alcohol to malic acid should be charged?
- What types of process control systems are required to ensure product quality?
- What are you going to do with the aqueous byproduct and the recovered excess alcohol?
- Is it worth buying any additional vessels for post-treatment, filtration, storage, etc.?
- What kind of vacuum system should you purchase?
- What equipment will be needed for filtration?
- What will your overall batch cycle time be?
Costs:
- Malic Acid, 1,000 kg supersacks, $2,750 each; 50 lb bags, $78 each
- 3-pentanol, 55 gal drums, $2.55/lb; 5000 gal tank truck @ $1.95/lb
- Sulfuric Acid, use market price
- Electricity, $0.05 per KWH.
- Cooling water, 90°F, $0.50/1,000 gal

Data & Additional Information:
- The viscosity (cP) of the reactor contents can be estimated using the equation $0.00211 \times \exp(2,600/T)$, where $T$ is in Kelvin.
- Product density is 1.03 g/cc. Assume that this is also the density of the reactor contents at every point in the reaction.
- Residual acidity can be measured by titration, requiring 15 minutes to obtain a measurement from the time the sample is taken. Residual alcohol and product purity are measured by chromatography, requiring 45 min from the time the sample is taken.

Use the following reaction rate expressions in your model, treating the two acid groups on each malic acid molecule as if they are two separate molecules:

$$\text{Acid} + 3\text{-Pentanol} = \text{Ester} + \text{Water}$$
$$2\text{Ester} = \text{Dimer} + 3\text{-Pentanol}$$

**Formation of ester:**
Rate (mol/L-min) = $1,000,000 \times \exp[-15,000/(RT)] \times [\text{Acid}] \times [\text{BuOH}]

**Back-Reaction:**
Rate (mol/L-min) = $1,000,000 \times \exp[-16,000/(RT)] \times [\text{Ester}] \times [\text{Water}]

**Byproduct (Dimer) Reaction:**
Rate (mol/L-min) = $10,000,000 \times \exp[-23,000/(RT)] \times [\text{Ester}]^2$

Make the following additional assumptions (and be sure to document additional assumption you make):
- Malic acid completely dissolves in 3-pentanol at 70°C.
- The heat capacity of the reactor contents is 0.50 Btu/lb°F throughout the process.
- Assume that the reaction occurs at atmospheric pressure.
- Assume that all products of neutralization are insoluble.
- Assume that during filtration only the resistance of the cake itself is significant.
- No additional equipment must be purchased to transport or charge the solid malic acid.
Figure 1. Reaction Schemes for Di(3-pentyl) Malate Manufacture
4. Nitrogen Rejection Unit  
(recommended by William B. Retallick, Consultant)

This unit is part of a gas plant, which prepares raw natural gas for sale to a pipeline. The front end of the gas plant has already removed the natural gas liquids from the gas. It remains for the rejection unit to remove nitrogen and also recover helium, a valuable by-product. Flow diagrams for the unit are included in a paper by Scott Troutmann, of Air Products and Chemicals, and Kim Janzen, of Pioneer Natural Resources. The unit uses two stripping columns. You can produce a side stream from the first stripping column that contains about 50 mol% nitrogen. This will be used to fuel the gas turbines, which drive the compressors.

The feed consists of two streams:

<table>
<thead>
<tr>
<th></th>
<th>Stream 1</th>
<th>Stream 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate, million SCFD</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Pressure, psig</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Helium, mol%</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>16.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Methane</td>
<td>balance</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>1.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Propane</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

1. Pipeline gas is to be delivered at 1,200 psig, containing no more than 2 mol% N₂.
2. Crude helium product contains at least 65 mol% helium, a maximum of 1 mol% methane, with the balance N₂, and is delivered at 1,200 psig. Recovery of helium is at least 96 mol%.
3. The selling price of crude helium is $25 per 1,000 ft³ of helium content.
4. When heat is transferred (irreversibly) with a temperature difference, ΔT, the lost work is $QΔT/T$, where T is the temperature of the warm fluid.

At cryogenic temperatures, where T is smaller, the losses are greater. Hence, to avoid increases in the lost work as T decreases, the minimum internal temperature difference (MITD) must be reduced. As you carefully select the MITD, consider the range of 1 - 6 K for your design.
5. Simplify your calculations with the units K, kg and atm.
6. Purchased electricity costs $0.70 per kWh.
7. The plant is located in Texas.
8. The cryogenic vessels and exchangers are of 304L stainless steel.

9. The heat exchangers are plate exchangers.

10. You can display the economics of your process by graphing the investor’s rate of return (IRR) as a function of the cost of the feed divided by the sales price of the gas.

Reference:


5. Ultra-low Sulfur Diesel Fuel
(recommended by Selma Kwok, Alex Bolkhovsky, and Heather Cochrane, Exxon/Mobil)

With increasing pressure from the government to improve fuel quality, many gasoline producers are faced with technical and economic challenges to meet the new specifications. One area of specific interest is the new-ultra low sulfur specification for U.S. on-road diesel fuel. By 2006, refiners are expected to decrease the sulfur content of highway diesel fuel from 500 ppmV to 15 ppmV.

Your refinery, which is located in Louisiana, currently runs a hydrotreater (HTR 1) that uses the Standard HTR Catalyst and processes the kerosene, diesel and vacuum gasoline oil cuts of East Texas Medium Crude Oil to produce 30,000 BPSD of diesel fuel. The proportion of kerosene to diesel to vacuum gasoline oil cuts is 3:6:1. The amount left of each cut can be sold on the open market. HTR 1 reduces the sulfur level from 1 wt% to 500 ppmV. You are faced with the tight sulfur specification that will take effect in 2006. You must find a viable option to reduce the sulfur level, or be pushed to sell your diesel product as a low-value fuel or decrease your output of diesel fuel based on the blend of the three cuts of the crude oil.

Your team of planning and technical experts has reported the following options to reduce the sulfur content in the diesel fuel:

1) Another hydrotreater can be added to treat the product from HTR 1 to reduce further the sulfur content. The new type of catalysts ("Improved Catalyst A or B") can be used to reduce the level of sulfur to 15 ppmV in both reactors. (Catalyst information is listed below.)

2) You may buy the kerosene, diesel and vacuum gasoline cuts of the Brent crude as feed for the hydrotreater. The proportion of kerosene to diesel to vacuum gasoline oil cuts is 3:6:1. The amount left of each cut can be sold on the open market. However, the crude is only available for 9 out of 12 months. For the other 3 months, you may
process the East Texas Medium Crude Oil and sell the product as low-value fuel, or shut the unit down.

3) You may use the Fischer-Tropsch Process to produce the diesel fuel.

Catalyst Information:

<table>
<thead>
<tr>
<th>Catalyst Information</th>
<th>Price</th>
<th>Down Time Required Between Cycles</th>
<th>Catalyst Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard HTR Catalyst</td>
<td>$ 3.50</td>
<td>3 days</td>
<td>1 year</td>
</tr>
<tr>
<td>Improved HTR Catalyst A</td>
<td>$ 4.50</td>
<td>3 days</td>
<td>1 year</td>
</tr>
<tr>
<td>Improved HTR Catalyst B</td>
<td>$ 8.25</td>
<td>5 days</td>
<td>1.5 years</td>
</tr>
<tr>
<td>Fischer Tropsch Catalyst</td>
<td>$20.00</td>
<td>6 days</td>
<td>2 years</td>
</tr>
</tbody>
</table>

Reaction Information:

<table>
<thead>
<tr>
<th>Catalyst Information</th>
<th>H2 Consumption (SCFH/BBL Fd)</th>
<th>Sulfur Conversion (Prod-Fd)/Fd</th>
<th>Operating Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard HTR Catalyst</td>
<td>300</td>
<td>0.94</td>
<td>600-900 psig</td>
</tr>
<tr>
<td>Improved HTR Catalyst A</td>
<td>320</td>
<td>0.97</td>
<td>600-900 psig</td>
</tr>
<tr>
<td>Improved HTR Catalyst B</td>
<td>350</td>
<td>0.99</td>
<td>800-1,100 psig</td>
</tr>
<tr>
<td>Fischer Tropsch Catalyst</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

References:

Information on the crude oil can be found at:

http://www.exxonmobil.com/crude_oil/
http://www.oilprices.com
http://www.eia.doe.gov/oiaf/servicerpt/ulsd


6. Rapamycin-coated Stents for Johnson & Johnson
(recommended by Scott L. Diamond, U. Penn)

In the treatment of heart disease, a common procedure involves balloon angioplasty to expand a narrowed coronary artery followed by placement of a metal support called a stent to keep the vessel open. Stenting helps reduce vessel closure, a process called restenosis. However, even stented vessels can undergo restenosis. There were 926,000 angioplasties in the U.S. in 1998 and 800,000 angioplasties outside the U.S. in 1999. Johnson & Johnson recently finished a clinical trial with polymer-coated stents that slowly release the drug rapamycin. In 238 patients in Europe, not a single patient had restenosis after 6 months with the rapamycin-coated stents. Johnson & Johnson is positioned to obtain over 50% market share in the highly competitive stent market.
Production Criteria

1) Produce and purify medical grade Sirolimus (rapamycin) via batch bioprocessing using streptomyces fermentation. Determine how much rapamycin you must produce annually and how many batches will be necessary.

2) You will be provided with the metal stents from the Stent Manufacturing Group. You will carry out the drug-polymer coating of the stents and deliver the drug-polymer coated stents to the Catheter Manufacturing Group on a monthly basis.

3) You will buy pure medical-grade speciality chemical components for the polymer coating, but must develop the coating technology to achieve the correct drug loading and release characteristics needed in the clinical application. You will have to design a spray-coating process using ultrasonic nozzles as well as a drying process to remove the solvent. Solvent recovery is also required. Degradable polymers will include \( \varepsilon \)-caprolactone-co-glycolic acid.

4) Manufacture:
   - 500,000 drug-polymer coated stents in year 1
   - 1,500,000 drug-polymer coated stents in year 2 and after.

5) Estimate the capital cost and annual operating cost of the drug manufacture and coating systems.

References:

- www.uspto.gov patent 6,153,252
  patent 6,273,913


7. Recombinant Hepatitis B Vaccine
(recommended by Eric T. Boder, U. Penn.)

Background:

Recombinant Hepatitis B (HB) vaccines have been widely used in the U.S. since the late 1980’s when a process for production of virus-like particles was developed (U.S. Patent 4,816,564). These particles, though not perfect mimics of natural Hepatitis B particles isolated from the serum of infected carriers, are capable of inducing long-term, protective immunity when administered in three doses of 5µg each over the course of several months. In 1991, the Centers for Disease Control recommended vaccination of all children in the U.S., and subsequently most states have legislated mandatory vaccinations for all children prior to school attendance. Thus, the two recombinant vaccines from Merck (Recombivax) and Glaxo-SmithKline (Engerix) have enjoyed great sales success and are considered among the flagship products for these pharmaceutical manufacturers. Legislated requirements for HB vaccination imply strong future demand for recombinant vaccines.

Recombinant HB vaccines are associated with adverse reactions in up to 17% of those receiving the vaccine. The current HBV particle production process uses the baker’s yeast *Saccharomyces cerevisiae* as the heterologous protein expression host. These yeast-produced particles have been observed to contain entrapped carbohydrates. Carbohydrate structures synthesized by yeast differ chemically from those synthesized in mammalian cells; these chemical differences often induce strong carbohydrate-specific immunological reactions in humans and may be related to the frequency of adverse side effects in HBV vaccinations. In addition, antibodies against yeast carbohydrates are likely to be present in any immunized individual due to prior exposure to environmental yeast. Recognition of these entrapped carbohydrates by antibodies reduces the effectiveness of the vaccine.

Recently, HBV particles have been expressed in a yeast strain deficient in enzyme pathways responsible for glycosylation (mnn9 mutant strain). HBV particles synthesized in this strain have been shown to contain 10-fold less entrapped carbohydrate. You are considering bidding for a contract to produce a new version of HBV vaccine with lowered carbohydrate content. Merck sells each 5 µg dose of Recombivax for $30. To compete for this contract, you must be able to supply 300 g per annum of vaccine at a cost of $0.50/dose or less. Due to limited shelf life, you will need to provide monthly shipments of material to Merck for packaging.

Process:

You will produce HBV particles intracellularly in yeast in a batch process. The protein products are toxic to the host cells; therefore, you will need to use an inducible expression system -- the GAL1/10 promoter system.
Biomass will first be grown in glucose medium, followed by galactose-mediated induction of protein expression.

Yeast cells will be harvested and lysed and total protein collected.

HBV protein can be purified either by immunoaffinity chromatography or wide-pore silica chromatography. Immunoaffinity chromatography will require licensing of a monoclonal antibody-producing hybridoma cell line and contracting for a supply of antibody-coupled affinity resin.

You will be required to validate that your product is >98% pure and contains no more than 0.05 mg carbohydrate/mg protein. Also, each batch must be monitored for contamination; contaminated fermentations must be discarded.

You have negotiated a license for the mnn9 yeast strain at a cost of 2% of gross annual sales. This strain has been determined to produce approximately 100 µg purified HBV protein per liter of culture.

Your process should have the following major steps:

1. Shake flask or small scale bioreactor culture of yeast to produce an innoculum from a master cell bank.
2. Bioreactor fermentation of yeast for HBV protein production.
3. Cell disruption and removal of debris by centrifugation or microfiltration.
5. Purification of HBV particles.
6. Dialysis and concentration of product.

Evaluate the costs of producing pure HB vaccine and determine the economic feasibility of bidding for this contract.

Reference:

U.S. Patent 4,816,564
PCTFE (polychlorotrifluoroethylene) is an inert polymer used to make packaging film for pharmaceutical applications and protective coatings. PCTFE film provides unsurpassed resistance to water vapor transmission so that water sensitive pharmaceutical products can be protected from degradation in clear push through packaging known popularly as "blister packs".

Traditionally, the monomer, chlorotrifluoroethylene, is converted by emulsion or suspension polymerization in water as described in the Encyclopedia of Polymer Science and Engineering, Wiley, Vol. 3, pp. 463-491 (1985). Frequently, copolymers of CTFE and vinylidene fluoride are also used in the same applications and are polymerized using the same methods. However, the batch nature of these processes and the subsequent processing steps to remove and dispose of contaminated water impose quality and economic costs that have spurred research into other polymerization and recovery methods. Among these are Professor Joseph DeSimone's research efforts to polymerize tetrafluoroethylene, CTFE and other monomers using supercritical CO₂ as the reaction medium and traditional organic peroxides as the source of free radical initiator (DeSimone, Joseph M., U.S. Patent 5,618,894 to University of North Carolina, April 8, 1997). This new approach offers the potential to improve quality and reduce costs by allowing continuous polymerization of the monomer(s), by facilitating removal of reaction medium by evaporation at suitably reduced pressure, and recovery of the product directly as a dry powder.

The goal of the study would be to determine the most economic arrangement of unit operations to perform the supercritical CO₂ polymerization starting from liquid monomers under pressure at atmospheric temperature and ending with final polymer in powder form. Honeywell engineers would be available for guidance and suggestions. Data on CTFE monomer are available from Honeywell and from the NIST web book at http://webbook.nist.gov/chemistry.

References:


U.S. Patent 5,618,894

Methyl methacrylate (MMA) is a monomer or comonomer in many polymers, most notably Plexiglas (R). The conventional MMA process has many drawbacks, including use of sulfuric acid as a catalyst. Most manufacturers neutralize the sulfuric acid with ammonia, producing byproduct ammonium sulfate, which must be sold or disposed of. HCN is also used in the process, requiring the MMA plant to be linked to a source of highly toxic HCN.

Ineos Acrylics UK Ltd., who bought ICI’s acrylics business, is commercializing a new route to MMA that eliminates the above problems. Their process carbomethoxylates ethylene to form methyl propionate (MP) using a homogeneous palladium catalyst. MP is then reacted with formaldehyde in the gas phase, giving MMA and water. Both reactions are highly selective. The MMA will then need to be purified to meet normal commercial specifications.

\[
CH_2 = CH_2 + CO + CH_3OH \rightarrow CH_3 - CH_2 - COO - CH_3 \\
(MP)
\]

\[
CH_3 - CH_2 - COO - CH_3 + CH_2O \rightarrow CH_3 - C = CH_2 + H_2O \\
\mid \\
COO - CH_3 \\
(MMA)
\]

Your company has asked your group to determine whether this new technology should be used in your Gulf Coast plant. Your job is to design a process and plant to produce 200 MM lb/yr of MMA from ethylene, which is available on the site. Based on past experience, you know that you will have to be able to defend any decisions you have made throughout the design, and the best defense is economic justification.

Your manager has hinted to you that an outstanding report, one that will guarantee your next promotion, will include the effects of the reversible, equilibrium oligomerization of formaldehyde in the plant simulation. If she wanted formaldehyde treated simply, as just a monomer, she would not have assigned your team to the project.

Assume a U.S. Gulf Coast location on the same site as a large chemical plant. 99.95% pure MMA can be sold for $0.60/lb, according to your marketing organization. Ethylene is available on your site for $0.23/lb. Formaldehyde sells for $0.20/lb of contained formaldehyde, and can be bought as a 37% solution in water, with 15% methanol to stabilize the monomer. Carbon monoxide can be purchased over the plant fence for $0.12/lb at 100 psig. Methanol is estimated by your marketing organization to cost $0.40/gal over the long term. However, if MTBE is legislated out of gasoline, that price might drop to $0.20/gal, while the price of formaldehyde, made from methanol, might
drop to $0.16/lb. Test your economics with both sets of prices, and make appropriate recommendations. All prices listed are in 2002 dollars.

The plant design should be as environmentally friendly as possible. Recover and recycle process materials to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate. Remember that you will be there for the start-up and will have to live with whatever design decisions you have made.

References:

World Patents 99/21820, 99/52628, 99/02480 to ICI

10. Acetaldehyde from Acetic Acid

Acetaldehyde is a versatile chemical intermediate. It is commercially made via the Wacker process, the partial oxidation of ethylene. That process is very corrosive, requiring expensive materials of construction. And like all oxidations, over-oxidation of the ingredient and the product reduce the yield, and convert expensive ethylene into carbon oxides.

Acetic acid, produced from inexpensive methanol, would be a good feedstock, if a selective route to acetaldehyde could be found. Because of the possible legislation of MTBE out of gasoline, there may be a worldwide glut of methanol, so any chemicals that use methanol may become much more economically attractive. But the reduction of acetic acid to acetaldehyde is notoriously difficult, because aldehydes are easier than acids to reduce.

However, Eastman Chemical has developed a selective palladium catalyst that gives acetaldehyde with selectivity of up to 86% at 46% conversion. Byproducts formed include ethanol, acetone and ethyl acetate, all of which can be sold after purification.

\[ \text{CH}_3-\text{COOH} + \text{H}_2 \rightarrow \text{CH}_3-\text{CHO} + \text{H}_2\text{O} \text{ (main reaction)} \]

\[ \text{CH}_3-\text{COOH} + 2\text{H}_2 \rightarrow \text{CH}_3-\text{CH}_2\text{OH} + \text{H}_2\text{O} \]

\[ \text{CH}_3-\text{COOH} + \text{CH}_3-\text{CH}_2\text{OH} \leftrightarrow \text{CH}_3-\text{COO}-\text{CH}_2-\text{CH}_3 + \text{H}_2\text{O} \]

\[ 2 \text{CH}_3-\text{COOH} + 2\text{H}_2 \rightarrow \text{CH}_3-\text{CO}-\text{CH}_3 + \text{CH}_4 + \text{H}_2\text{O} \]

Distillation of the product will be complicated by the existence of azeotropes between ethanol and ethyl acetate, water and ethanol, and water and ethyl acetate. And the acetic
acid-water and acetone-water mixtures are famous for their tangent pinches. Rigorous distillation simulations with thermodynamics that accurately predict each of these azeotropes and pinches will be required to have confidence in the design.

Your company has asked your group to determine whether this new technology should be used in your Gulf Coast plant. Your job is to design a process and plant to produce 100 MM lb/yr of acetaldehyde from acetic acid, which is available on the site. Based on past experience, you know that you will have to defend any decisions you have made throughout the design, and the best defense is economic justification.

Assume a U.S. Gulf Coast location on the same site as a large chemical plant. Acetaldehyde can be sold for $0.48/lb, according to your marketing organization. Acetic acid is available on your site for $0.16/lb. However, if MTBE is legislated out of gasoline, that price might drop to $0.12/lb. Test your economics with both prices, and make appropriate recommendations. Hydrogen can be purchased over the plant fence for $0.50/lb at 200 psig. Ethanol, if 99.95% pure, can be sold (on an excise tax-free basis) for $2.50/gal; however, the ethanol-water azeotrope can also be sold into the fuel market for $1.60/gal. You may sell either or both grades of ethanol, depending on which is most economical to produce. Ethyl acetate can be sold for $0.60/lb. Acetone can be sold for $0.20/lb. You will need storage tanks, truck or railcar loading stations, etc., for each byproduct that you sell, or you may burn them in the boiler for fuel value. Byproducts sold must also meet normal purity specs for that chemical. All prices listed are in 2002 dollars.

The plant design should be as environmentally friendly as possible. Recover and recycle process materials to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate. Remember that you will be there for the start-up and will have to live with whatever design decisions you have made.

References:

US Patent 6,121,498 to Eastman Chemical.
11. Diphenyl Carbonate

Polycarbonates, particularly valued for their optical clarity and impact resistance, have historically been made using highly toxic phosgene. Recently, they have been made via the transesterification of diphenyl carbonate (DPC) with bisphenol A. But the production of DPC has been problematic. The conventional route to DPC also uses phosgene, while another route has troublesome azeotropes.

Mitsubishi Gas Chemical has developed a new route where inexpensive urea reacts with n-butanol, to produce first butyl carbamate (BC) and then dibutyl carbonate (DBC). The DBC must then be purified before it can be reacted with phenol to give phenyl butyl carbonate (PBC). PBC can then be disproportionated to DPC and DBC.

\[
\text{NH}_2 - \text{CO} - \text{NH}_2 + \text{BuOH} \rightarrow \text{NH}_3 + \text{NH}_2 - \text{CO} - \text{OBu} \quad (\text{BC})
\]

\[
\text{NH}_2 - \text{CO} - \text{OBu} + \text{BuOH} \rightarrow \text{NH}_3 + \text{BuO} - \text{CO} - \text{OBu} \quad (\text{DBC})
\]

\[
\text{BuO} - \text{CO} - \text{OBu} + \text{PhOH} \rightarrow \text{BuOH} + \text{PhO} - \text{CO} - \text{OBu} \quad (\text{PBC})
\]

\[
2 \text{PhO} - \text{CO} - \text{OBu} \rightarrow \text{BuO} - \text{CO} - \text{OBu} + \text{PhO} - \text{CO} - \text{OPh} \quad (\text{DPC})
\]

At first glance, this process would also appear to have problems, since BC and DBC form an azeotrope which must be broken before the reaction with phenol. However, Mitsubishi found that phenol itself could be used to break the azeotrope. Phenol and DBC distill overhead, leaving BC in the bottoms, which can be recycled. The phenol-DBC stream can then be reacted to form PBC, liberating n-butanol for recycle.

Your company has asked your group to determine whether this new technology should be used in your Gulf Coast plant. Your job is to design a process and plant to produce 100 MM lb/yr of DPC from urea and phenol. Based on past experience, you know that you will have to defend any decisions you have made throughout the design, and the best defense is economic justification.

Assume a U.S. Gulf Coast location on the same site as the polycarbonate plant. This site does not currently produce “chemicals”, so you will have to provide all utilities required (boiler, cooling water, etc.). Other outside battery limits investment will be higher than normal also.

Urea sells for $150/ton, according to your marketing organization. Phenol can be purchased for $0.28/lb. Butanol can be purchased for $0.50/lb. Your company currently purchases its DPC from a competitor for $0.75/lb. Ammonia byproduct can be sold for $200 per ton if it is anhydrous. You may also buy sulfuric acid for $25 per ton to neutralize aqueous ammonia, then crystallize and dry the ammonium sulfate (AS), and sell it for $100 per ton in bulk. You may make and sell anhydrous ammonia or AS or
both, or do anything else with the ammonia that is environmentally sound, whichever you decide is most economical. All prices listed are in 2002 dollars.

Your competitor, who wants to keep its plant running at full capacity, is likely to offer you a lower price on the DPC if they believe that you are serious about building your own plant. Calculate the DPC price that they would have to offer you in order for your company to be indifferent between making and buying DPC. In other words, calculate the DPC price that makes the net present value (NPV), discounted at your company’s opportunity cost of capital of 25%, of buying DPC equal to the NPV of making DPC yourself. Even if you decide not to build the plant, your company may make some money with this technology by vendor torquing. Calculate the NPV of the technology if it forces your competitor to reduce your DPC price to the indifference point.

The plant design should be as environmentally friendly as possible. Recover and recycle process materials to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate. Remember that you will be there for the start-up and will have to live with whatever design decisions you have made.

References:

US Patents 6,169,197, 6,031,122, 5,980,445, and 5,714,627 to Mitsubishi Gas Chemical.