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This appendix contains the problem statements for 93 design projects, each prepared for design teams of three or four students at the University of Pennsylvania by chemical engineers in the local chemical industry and by the chemical and biomolecular engineering faculty. At Penn, each team selects its design project during the first lecture course in the fall, and spends the spring semester completing the design. In the spring, each group meets regularly with its faculty advisor and industrial consultants, including the individual who provided the problem statement, to report on its progress and gain advice.

The problem statements in the file, Appendix IIS.pdf, on the CD-ROM are in their original forms, as they were presented to the student design teams on the date indicated. Some provide relatively little information, whereas others are fairly detailed concerning the specific problems that need to be solved to complete the design. The reader should recognize that, in nearly every case, as the design team proceeded to assess the problem statement and carry out a literature search, the specific problems it formulated were somewhat different than stated herein. Still, these problem statements should be useful to students and faculty in several respects. For students, they should help to show the broad spectrum of design problems that chemical engineers have been tackling in recent years. For the faculty, they should provide a basis for similar design projects to be created for their courses.

In formulating design problem statements, the industrial consultants and faculty strive to create product and process opportunities that lead to designs that are timely, challenging, and offer a reasonable likelihood that the final design will be attractive economically. Every effort is made to formulate problems that can be tackled by chemical engineering seniors without unduly gross assumptions and for which good sources of data exist for the reaction kinetics and thermophysical and transport properties. In this respect, this was accomplished in each of the problems included herein; furthermore, successful designs were completed by a student design team for most of these problems.

As seen in the contents, the projects have been assigned to one of the following areas, in some cases arbitrarily: Chemicals, Fuel Products, Gas Manufacture, Foods, Pharmaceuticals, Biomedical, Polymers, Electronic Materials, and Environmental.

Most of the problem statements focus on process design (PROC), although in recent years, more emphasis is shifting toward product design (PROD). See especially the recent projects under Pharmaceuticals, Biomedical, and Electronic Materials.

Credit is given to each formulator on his/her problem statement. In addition, the names of the contributors are listed below with many thanks, as their contributions in preparing these design problems have been crucial to the success of the design course.

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A-IIS.1 CHEMICALS

A-IIS.1.1 Batch Di (3-pentyl) Malate Process [PROC]

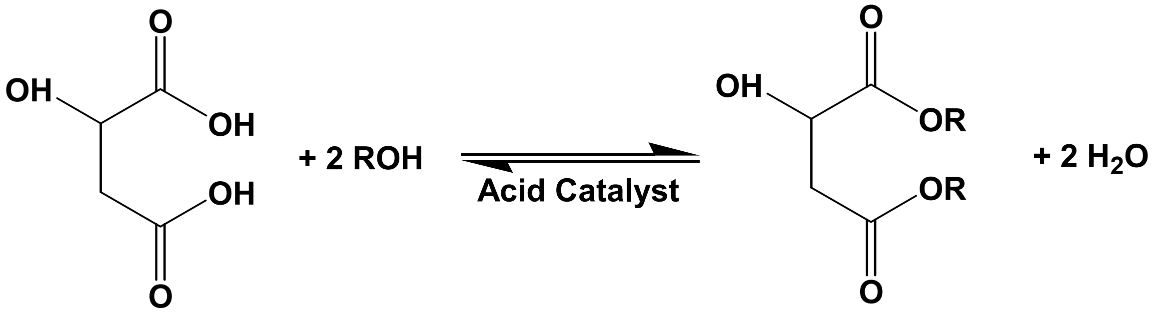
(Frank Petrocelli and Andrew Wang, Air Products and Chemicals, January 2002)

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:

Anticipated Sales (in thousands of pounds)

	1	*2*	*3*	*4 and beyond*
Sales @ \$6.50/lb	100	600	1,600	3,000
Sales @ \$8.00/lb	75	450	1,200	2,250

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 ft^2 and an estimated overall heat-transfer coefficient of 100 $Btu/ft^2hr°F$.



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 A-IIS.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 A-IIS.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 A-IIS.1. Finally, the product must be filtered to remove the salts of neutralization. Your company currently has no vacuum or filtration equipment.

Table A-IIS.1. Mass Transfer Data

$\frac{dx}{dt} = k_L a\left(y^* - y\right)$ 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 1,200 mm Hg.

Superficial Gas Velocity (scf/ft^2,min)	2	5	10	20	50
k_La (1/hr)	0.076	0.12	0.17	0.24	0.37

The required product specifications are:

Residual acidity (prior to neutralization)	<0.1N
Residual 3-pentanol	<0.1 wt.%
Purity (moles ester / total moles)	>98 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*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 measure 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:

Acid + 3-Pentanol = Ester + Water
2Ester = Dimer + 3-Pentanol

Formation of ester:
Rate (mol/L-min) = 1,000,000 exp[-15,000/RT]*[Acid][BuOH]
Back-Reaction:
Rate (mol/L-min) = 1,000,000 exp[-16,000/RT]*[Ester][Water]
Byproduct (Dimer) Reaction:
Rate (mol/L-min) = 10,000,000 exp[-23,000/RT]*$[\text{Ester}]^2$

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.

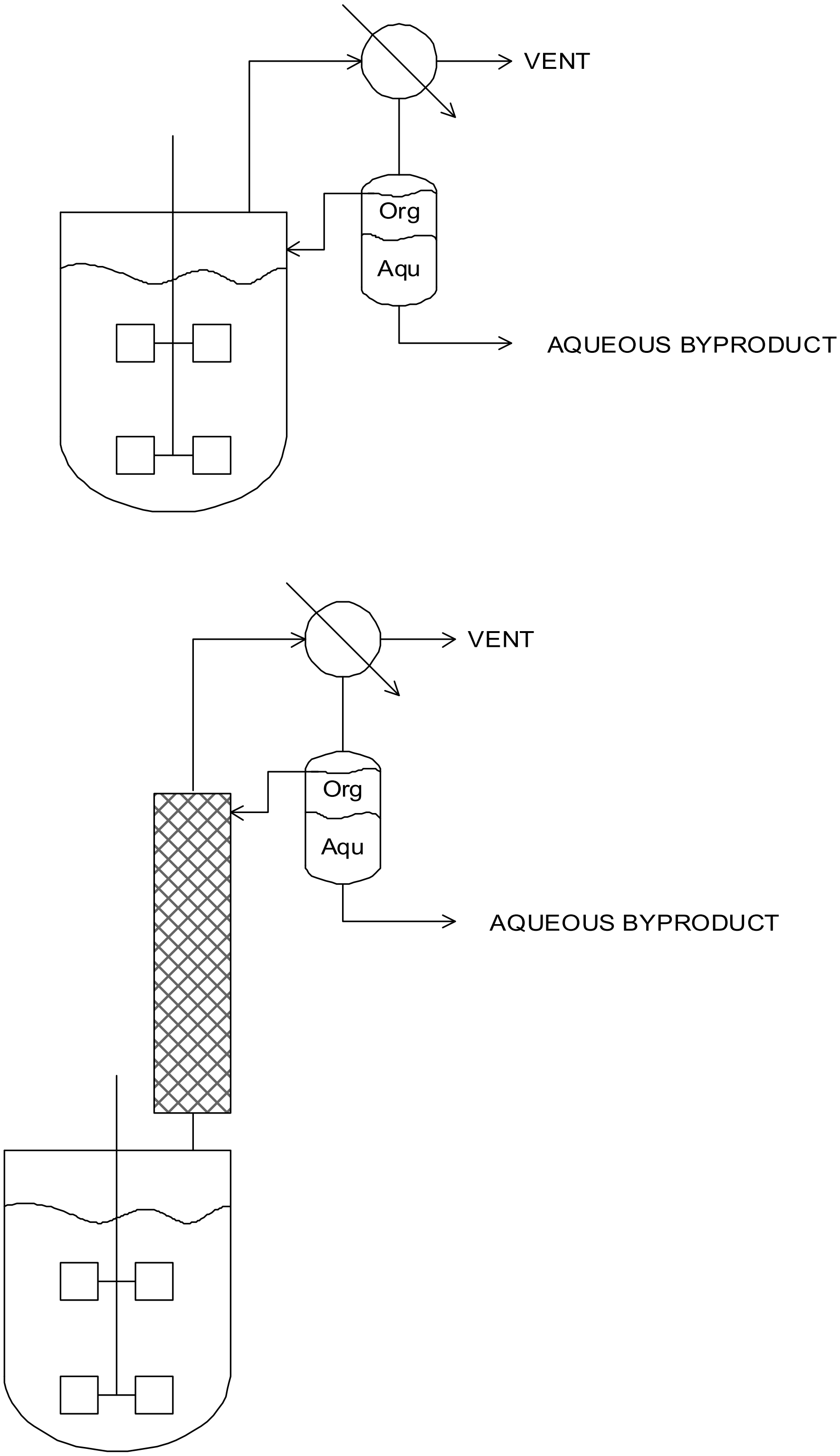


Figure A-IIS.1. Reaction Schemes for Di(3-pentyl) Malate Manufacture

A-IIS.1.2 Acetaldehyde from Acetic Acid [PROC]
(Bruce M. Vrana, DuPont, January 2002)

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.

$$CH_3-COOH + H_2 \rightarrow CH_3-CHO + H_2O \ (main\ reaction)$$

$$CH_3-COOH + 2H_2 \rightarrow CH_3-CH_2OH + H_2O$$

$$CH_3-COOH + CH_3-CH_2OH \leftrightarrow CH_3-COO-CH_2-CH_3 + H_2O$$

$$2\,CH_3-COOH + 2H_2 \rightarrow CH_3-CO-CH_3 + CH_4 + H_2O$$

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.

Reference

U. S. Patent 6,121,498 to Eastman Chemical.

A-IIS.1.3 Ethylene by Oxidative Dehydrogenation of Ethane [PROC]

(Bruce M. Vrana, DuPont, January 2001)

Ethylene is the largest volume organic chemical product, with world production over 50 billion pounds per year. It is normally produced by steam cracking of ethane or heavier hydrocarbons. This process is quite energy and capital intensive.

Dow Chemical has recently applied for a patent on a new process, which may require significantly less investment. In this process, ethane is passed over a catalyst at very high space velocity (100,000/hr or higher), and reacts with oxygen (exothermically!), producing ethylene in good selectivity (greater than 80% under some conditions) and high conversion. The selectivity is similar to that in the conventional steam cracking process, but the conversion is higher. Hydrogen in the feed improves the conversion while minimizing the over-oxidation of the feedstock.

Because the reaction with oxygen is exothermic, the expensive furnaces of the steam cracking process should not be required. Much less coke is produced in this reactor system, according to Dow, which should result in a much more operable plant.

Dow has patented both a fixed bed supported catalyst and a fluidized bed reactor. The fluidized bed has a slightly higher selectivity, and would probably be easier to manage the heat load than the less expensive fixed bed reactor. You should use economics and technical criteria to guide your decision about which reactor technology to use in the plant design, and discuss this major decision in your report.

Your company has 1 MMM pounds per year of ethane, which is currently being produced at your Gulf Coast plant and sold for $0.07/lb in 2000. Your team has been asked to evaluate the economic viability of the Dow process for your plant, as a way of upgrading your product and increasing your sales revenue. Your job is to determine the economic optimum design, maximizing the net present value (NPV) of the project. You may consume all or part of the ethane, which is available. 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 plant design must be backed up with a rigorous simulation of the entire process, with all recycle loops closed.

Your marketing organization believes they can sell ethylene for $0.25/lb in 2001 dollars. Pipeline oxygen in your area costs $0.02/lb. It would be a good idea to test the sensitivity of the optimum plant design and economics to uncertainty in the selling prices of the product and the raw material.

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, an important consideration with oxygen and hydrocarbons. Remember that you will be there for the start-up and will have to live with whatever design decisions you have made.

Reference

World Patent Applications 00/14035 and 00/14180 to Dow.

A-IIS.1.4 Butadiene to n-Butyraldehyde and n-Butanol [PROC]

(Bruce M. Vrana, DuPont, January 2000)

n-Butyraldehyde is conventionally produced from propylene and highly toxic synthesis gas in the so-called oxo process. The n-butyraldehyde is used to make 2-ethyl hexanol via aldol condensation as well as n-butanol. These oxo alcohols are frequently used, in either the alcohols or ester form, as solvents.

Because propylene is frequently quite expensive and in short supply, BASF has applied for a patent on a new route to n-butyraldehyde and/or n-butanol starting from butadiene. They found that a homogeneous palladium acetonylacetonate catalyst with phosphine ligands would allow butadiene to react with n-butanol to produce 1-n-butoxy-2-butene (nBB). nBB will then react with more n-butanol to produce the acetal, using a homogeneous phosphine modified ruthenium catalyst. The acetal can be hydrolyzed to n-butyraldehyde, or hydrogenated and hydrolyzed to n-butanol using the same Ru catalyst.

$$CH_2{=}CHCH{=}CH_2 + BuOH \rightarrow BuO\text{-}CH_2CH{=}CHCH_3 \quad [nBB]$$

$$nBB + BuOH \rightarrow (BuO)_2CHCH_2CH_3 \quad [Acetal]$$

$$Acetal + H_2O \rightarrow O{=}CHCH_2CH_2CH_3 + 2\ BuOH$$

$$Acetal + H_2 + H_2O \rightarrow 3\ BuOH$$

Unfortunately, in the first reactor, a side reaction produces 2-butoxy-3-butene (iBB). The iBB can be isomerized to nBB using an acid ion exchange resin or a Pd catalyst. Unfortunately, this isomerization reaction is likely to be equilibrium limited.

BASF also found that while this reaction works well with pure butadiene, it will also work with "crude" butadiene, the C4 olefin cut from an ethylene cracker. The butenes in the C4 cut are inert under the reaction conditions.

Your company has asked your group to determine whether this new technology should be used in your Gulf Coast plant, and if so, what the economic optimum feedstock and product would be. The goal is to maximize the net present value (NPV) of the project. 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 company has 200 MM lb/yr of crude butadiene, which is currently being burned for fuel value. Thus, one possible feedstock would be the butadiene contained in the crude. You would receive a credit for the unused C4's in the stream, so you would only have to pay fuel value for the butadiene you actually consume in the process. Of course, the inert C4's will dilute the reactor contents, making it larger, and complicate the separation train. As an alternative, you could purchase pure butadiene for $0.15/lb in 2001 dollars, which would result in smaller vessels.

The composition of your plant's C4 cut, which has already passed through your MTBE plant to react away the isobutylene, is:

43% BD
28% 1-butene
10% cis-2-butene
10% trans-2-butene
6% n-butane
3% isobutene

For a product, you could produce n-butyraldehyde or n-butanol, or some combination of the two. Your marketing organization believes they could sell the aldehyde for $0.40/lb, and n-butanol for $0.40/lb also, both in 2001 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.

Reference

World Patent Application 98/41494 to BASF

A-IIS.1.5 Methacrylic Acid to Methylmethacrylate [PROC]
(Bruce M. Vrana, DuPont, January 1999)

Methyl methacrylate (MMA) is a monomer or comonomer in many polymers, most notably Plexiglas (R). Although it is the methyl ester of methacrylic acid, it is not often produced from methacrylic acid.

BASF has recently patented a reactive azeotropic distillation process to produce esters from methacrylic acid and alcohols, involving a total of 3 columns. Although the patent example is for butyl methacrylate, they claim methyl methacrylate as well.

Design a process and plant to produce 100 MM lb/yr of MMA from methacrylic acid that your plant already produces. Use the process concept that BASF introduces, with appropriate modifications (improvements) for MMA.

Your process design must be supported by rigorous distillation simulations. VLE and LLE data are available in the DECHEMA Chemistry Data Series (Gmehling et al., 1980). Do not blindly use activity coefficients from a simulation program.

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. Assume a U.S. Gulf Coast location on the same site as a large oil and petrochemical plant. 99.95% pure MMA can be sold or transferred for \$0.60/lb, according to your marketing organization. The acid feed contains 5% water (by weight). Because it is impure, the cost of the acid in the stream is \$0.40/lb. Your marketing organization projects that the long-term average price of methanol is \$0.40/gal.

<u>References</u>

U.S. Patent 5,734,074 to BASF

Gmehling, J., U. Onken, W. Arlt, P. Grenzheuser, U. Weidlich, and B. Kolbe, Vapor-Liquid Equilibrium Data Collection, 13 Parts, DECHEMA, Frankfort, Germany (1980)

A-IIS.1.6 Coproduction of Ethylene and Acetic Acid from Ethane [PROC]
(Bruce M. Vrana, DuPont, January 2000)

Ethylene is the largest-volume organic chemical, with world production over 50 billion pounds per year. It is normally produced by steam cracking of ethane or heavier hydrocarbons. Acetic acid is another large-volume chemical, with annual world production in the billions of pounds. Acetic acid is normally produced using the Monsanto process from methanol and highly-toxic carbon monoxide, although there are some older technology plants still running.

Saudi Basic Industries (Sabic) has applied for a patent on a new catalyst which will coproduce ethylene and acetic acid from ethane and air. Their catalyst is a phosphorus-modified molybdenum-niobium vanadate. At different phosphorus levels, the catalyst will produce different ratios of ethylene to acetic acid. Selectivity to the two products is also a function of conversion (i.e., space velocity). As conversion increases, the selectivity to ethylene decreases and the selectivity to acetic acid increases. However, the total selectivity to the useful products decreases as conversion increases. The process runs at higher pressures, about 200 psig, than a conventional ethylene furnace.

Your company manufactures 2 MMM lb/yr of ethane which is currently being produced at your Gulf Coast plant and sold for $0.07/lb in 1999. Your team has been asked to evaluate the economic viability of the Sabic process for your plant, as a way of upgrading your product and increasing your sales revenue. Your job is to determine the economic optimum design, producing whatever products will maximize the net present value (NPV) of the project. You may consume all or part of the ethane which is available and make any ratio of ethylene to acetic acid which can be produced by the catalyst. 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.

Your marketing organization believes they can sell ethylene for $0.25/lb in 2000 dollars. Although they are less certain because it is a new product for your company, they also believe they can sell acetic acid for $0.19/lb in 2000 dollars. It would be a good idea to test the sensitivity of the optimum plant design and economics to uncertainty in the selling prices of both products.

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.

<u>Reference</u>

World Patent Application 99/13980 to Sabic

A-IIS.1.7 Methylmethacrylate from Propyne [PROC]

(Bruce M. Vrana, DuPont, January 1999)

Methyl methacrylate (MMA) is a monomer or comonomer in many polymers, most notably Plexiglas (R). The conventional process has many drawbacks, including the 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 hazardous HCN.

Shell has patented a new process with several advantages over conventional MMA processes. A major advantage is that neither HCN nor sulfuric acid are used. Shell found that propyne can be carbomethoxylated (reacted with CO and methanol) to produce MMA directly. The main disadvantage is that propyne is not normally considered a viable feedstock due to its scarcity and the impurities it contains. Shell's new catalyst tolerates impurities in the propyne much better than prior catalysts.

Your job is to develop a scenario for Shell to commercialize this process. You must first find a suitable feedstock for this process from the normal refinery and/or petrochemical streams available. Producing propyne to provide the feedstock is discouraged, due to high cost. Having found a stream which contains suitable quantities of propyne in high enough purity for this process to be feasible, design a plant to produce 100 MM lb/yr of MMA by the new Shell process. Determine the overall economic feasibility of the plant.

The plant design should be as environmentally friendly as possible. Recover and recycle process chemicals 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.

Assume a U.S. Gulf Coast location on the same site as a large oil and petrochemical plant. MMA can be sold or transferred for $0.60/lb, according to your marketing organization. Value the propyne as appropriate for alternative uses for the stream (i.e., if the stream you are using is normally burned, value the propyne at fuel value). A major gas vendor is willing to locate across the fence from you and supply CO at the required pressure for $0.12/lb. Your marketing organization projects that the long-term average price of methanol is $0.40/gal.

<u>Reference</u>

U.S. Patent 5,719,313 to Shell Oil Company

A-IIS.1.8 Mixed-C_4 Byproduct Upgrade [PROC]
(Leonard A. Fabiano and Robert Nedwick, Lyondell, January 1999)

Your company is a major player in commodity petrochemicals, specifically producing olefins via the cracking of ethane, propane, butane and naphthas. At one of your Gulf Coast sites, the major products are ethylene and propylene in addition to a number of smaller fuel streams. The crude C4 product, which because of the feed mix has been a relatively small portion of the product slate, is currently being sold at fuel value. Now, due to a change in feed mix, the C4 yield from the cracking furnaces has increased significantly. Management would like to upgrade this stream above fuel value. The expected feed composition and flow rate are as follows:

Composition	wt%
Methyl Acetylene	0.4
Propadiene	0.1
Propane	0.1
1,3 Butadiene	46.5
Ethyl Acetylene	0.1
Vinyl Acetylene	0.4
1-Butene	11.0
Cis-2-Butene	4.1
Trans-2-Butene	5.4
Iso-Butene	30.1
Iso-Butane	0.6
N-Butane	0.6
Iso-Pentane	0.6
Total	100.0
Flow rate, lb/hr	100,000

The company would like to maintain its focus on commodity chemicals and is interested in high volume products. Your project team has been assembled to determine:

1. What components are worth considering for recovery?

2. What processing options are available for the components of interest?

3. What is the most economical processing route?

and to develop a design package that will meet a 15% return on investment.

A-IIS.1.9 Hydrogen Peroxide Manufacture [PROC]
(Bruce M. Vrana, DuPont, January 1999)

Hydrogen peroxide is an oxidant used in many markets, including the pulp and paper industry. Almost all of the world capacity is based on alternately hydrogenating and oxidizing an expensive alkylanthraquinone.

Enichem has applied for a patent on a process based on oxidizing carbon monoxide in a complex aqueous solution. Rather than using expensive hydrogen, this process incorporates the hydrogen from water. The overall chemistry is:

$$CO + H_2O + O_2 \rightarrow H_2O_2 + CO_2$$

The application cites data with reactor productivities comparable to or even better than the conventional chemistry. Design a process and plant to produce 100 MM lb/yr of 50% H_2O_2 using this proposed reaction path.

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.

Assume a U.S. Gulf Coast location on a large plant complex. H2O2 can be sold or transferred for \$0.60/lb, according to your marketing organization, on a 100% basis. A major gas vendor is willing to locate across the fence from you and supply CO at the required pressure for \$0.12/lb and oxygen for \$0.02/lb.

Reference

European Patent Application 808796 by Enichem.

A-IIS.1.10 Di-tertiary-butyl-peroxide Manufacture [PROC]
(Leonard A. Fabiano, ARCO Chemical, January 1995)

It is desired to design a process to produce 100 million pounds per year di-*tertiary*-butyl-peroxide (DTBP) based primarily on a Texaco patent. DTBP is an important chemical that has use, for example, as a catalyst in various organic syntheses and has special utility as an additive to diesel fuel formulations to improve its combustion characteristics. It behaves in an analogous way to diesel fuel as octane enhancers (e.g., MTBE) behave in gasoline (see U.S. Patent 5,312,998, column 1, lines 29-33). The product must contain less than 0.3 weight percent tertiary-butyl-alcohol (TBA) and essentially no other peroxides. The plant will be constructed at a Gulf Coast location adjacent to a feedstock-producing facility. Texaco and ARCO have facilities in this area.

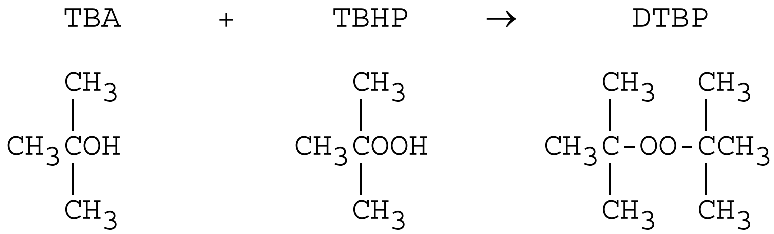
Specific kinetic data are not available but hourly space velocities are provided in the Texaco patent (80-100°C, 1-2 vol. TBHP per vol. catalyst per hour – U.S. Patent 5,345,009, column 4, lines 23-44). Phase equilibrium data are to be developed from the DIPPR databank and UNIFAC estimates using ASPEN PLUS.

Specifics

Your group is requested to develop and analyze a process to produce DTBP based on information provided in U.S. Patent 5,345,009 assigned to Texaco Chemical Company, and U.S. Patents 5,288,919 and 5,312,998 assigned to ARCO Chemical Company.

Assistance will be provided in making decisions, but will be very specific with references in the open patent literature. It should be apparent in this problem statement of this most timely process study that I must be careful not to release proprietary information which is contained in a very recent patent application for which I am one of the inventors. The results of this comparison of the Texaco process, as devised by your group, with the ARCO process is typical of an exercise that all companies must undertake to analyze the economic viability of all new ventures.

We are interested in comparing the Texaco technology with the *confidential* process developed by ARCO. However, you are expected to be very creative and devise a continuous process to minimize costs. It is suggested that you focus on Texaco patent (5,345,009 - column 2, lines 65 to the end, and column 3, lines 1-6). Paraphrasing, di-*tertiary*-butyl-peroxide (DTBP) is formed when *tertiary*-butyl-hydroperoxide (TBHP) and an enhanced amount of *tertiary*-butyl-alcohol (TBA) are brought into contact with a palladium-coated, carbon catalyst; that is,



$$\underset{\mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{OH}}{\text{TBA}} \quad + \quad \underset{\mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{OOH}}{\text{TBHP}} \quad \rightarrow \quad \underset{\mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{-OO-}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_3}}{\text{DTBP}}$$

ARCO Patent 5,288,919 (column 1, lines 5-11) suggests alternatively:

$$\text{TBA} + \text{Isobutylene } (iC_4^=) + \text{TBHP} \rightarrow \text{DTBP}$$

The two routes above are basically the same since TBA under the proper conditions and in the presence of a catalyst reacts to form isobutylene and water according to the reversible reaction:

$$\text{TBA} = iC_4^= + \mathrm{H_2O}$$

The isobutylene is the molecule that reacts directly with the TBHP.

ARCO Patent 5,312,998 (column 3, lines 31-40) offers the same possibilities. TBHP is catalytically reacted with TBA to form DTBP. Isobutylene can be added to the reaction mixture and it is generally advantageous to use a substantial excess of TBA and/or iC_4 relative to the TBHP to achieve high TBHP conversion; e.g., 90% or more. Conditions for the reaction (with different catalysts) are proposed in U.S. Patent 5,345,009 (column 4, lines 24-33). The reaction may be conducted at a temperature within the range of about 40˚C to about 160˚C at super-atmospheric pressures. A contact time of about 0.5-10 hours is required. U.S. Patent 5,288,919 (column 2, lines 19-29) suggests temperatures ranging from 20-150˚C at a sufficient pressure to ensure a liquid-phase reaction.

U.S. Patent 5,312,998 (column 2, lines 5-19) suggests that there can be a two-liquid phase reaction carried out in the temperature range of about 70-110˚C.

Similarities - Despite the Differences in Catalysts

U.S. Patent 5,345,009 (column 3, lines 15-29) suggests a typical feed stock for the Texaco process, but specifics of other components are not described. U.S. Patent 5,288,919 (column 3, lines 29-39) suggests a typical *debutanized* feed stock composition of 58 weight % TBA and 40 weight % TBHP, with the remainder comprised of 0.2% methanol, 1.3% acetone, and 0.5% water. For the Texaco process, let's use a mixture of 70% TBA, 30% TBHP and assume that this mixture makes up 98% of the mixture based upon the ARCO patent. The remaining 2% is assumed to be as above.

Note that TBA and DTBP, as well as TBA and water, form azeotropes.

Let's brainstorm and develop several likely candidate processes to evaluate and perhaps compare before we embark on detailed evaluations.

Alternative Process

ARCO produces TBHP-70, a possible "purified" feedstock for the reaction:

$$\text{TBHP} + iC_4^{=} \rightarrow \text{DTBP} + \text{TBA}$$

TBHP-70 is essentially 70% TBHP and 30% water. Would this provide an economically viable process?

<u>References</u>

U.S. Patent 5,345,009 (September 6, 1994).
U.S. Patent 5,288,919 (February 22, 1994).
U. S. Patent 5,312,998 (May 17, 1994).

A-IIS.1.11 Vinyl Acetate Process [PROC]
(Björn D. Tyreus, DuPont, January 1997)

Our company, BCI (Better Chemicals Inc.) has recently discovered a new product which we intend to manufacture in the near future. This product uses vinyl acetate as one of the main raw materials. We expect to use 300 MM PPY of vinyl acetate in our new process. In reviewing the economics of our new product, we found that it was negatively impacted by the relatively high market price of vinyl acetate ($0.44/lb). A closer investigation showed us that the most popular route to vinyl acetate is from ethylene and acetic acid oxidized by oxygen. The site where our new process will be constructed happens to use all three ingredients needed for vinyl acetate. Very favorable, long term contracts for their use have been negotiated. We thus find that we can obtain large quantities of acetic acid for $0.27/lb and ethylene for $0.20/lb. Oxygen costs us $0.02/lb. With these raw material prices, we feel that we can manufacture vinyl acetate far below the market price of $0.44/lb and thus make our new product that much more profitable. In assessing the project to manufacture our own vinyl acetate, we used some approximate estimating techniques [1] to evaluate the investors rate of return we could expect from a 300 MM PPY vinyl acetate plant as a function of the onsite capital investment. In these calculations, the onsite cost consists of the installed cost of all process equipment within battery limits. We estimate the offsite cost to be 45% of the onsite cost and apply a 25% contingency such that the fixed capital is related to the onsite cost as

$$\text{Fixed Capital} = 1.25\ (\text{onsite} + 0.45\ \text{onsite})$$

The results of our venture guidance calculations are shown in the figure below

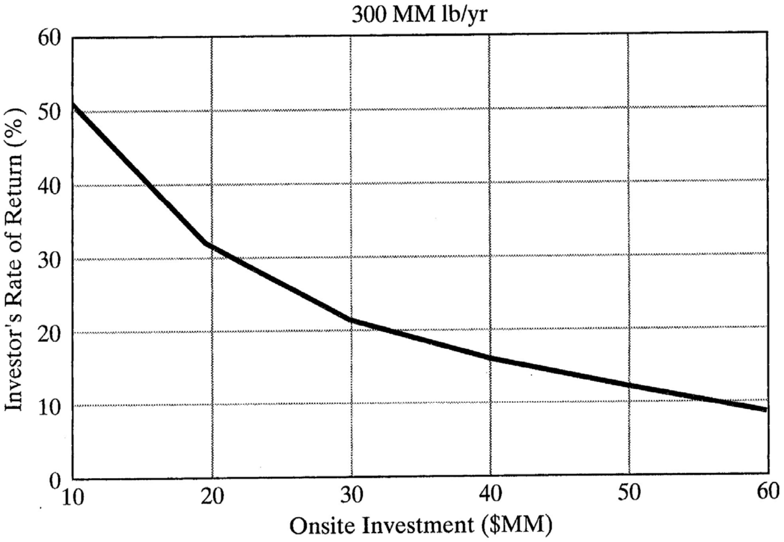


Figure A-IIS.2

While we do not know exactly how much we need to invest into the vinyl acetate process (this is one of the questions we have for you), we crudely estimate it to be less than $50-60 MM onsite. Since the cost of capital is 12%, we therefore expect this to be a profitable venture.

We now turn to the technology of the vinyl acetate process. Reference [2] gives an overview of the process and states that the main reaction is

$$H_2C = CH_2 + CH_3COOH + 1/2O_2 \rightarrow H_2C = CHOOC\text{-}CH_3 + H_2O \qquad \textbf{(R1)}$$

Reference [2] also indicates that the most economic route to vinyl acetate, when acetic acid is available, is to convert the raw materials to product in the vapor phase over a palladium catalyst. We therefore asked our research chemists to develop a catalyst suitable for the operation. They found a suitable catalyst by impregnating a silica base with 2% palladium along with some other proprietary chemicals. The chemists performed numerous experiments with the catalyst and found that it is quite selective towards vinyl acetate and quite active as measured in its space time yield (STY, grams of vinyl acetate/hr per liter of catalyst). The only significant side reaction we could notice is the combustion of ethylene to carbon dioxide and water

$$H_2C = CH_2 + 3O_2 \rightarrow 2CO_2 + 2\ H_2O \qquad \textbf{(R2)}$$

Once the catalyst was developed our chemical engineers designed a kinetic study using a laboratory-scale reactor to quantify the performance of the catalyst for the purpose of designing a commercial-scale reactor. For commercial purposes the catalyst support will be pelletized such that the bulk average density of the final catalyst is 30 lb/ft^3. The following rate expressions were obtained:

For R1:

$$r_1 = 0.1036 e^{-3,674/T} \frac{p_{O_2} p_{C_2^=} p_{HAc} \left(1 + 1.7 p_{H_2O}\right)}{\left(1 + 0.583 p_{O_2} \left(1 + 1.7 p_{H_2O}\right)\right)\left(1 + 6.8 p_{HAc}\right)} \left[\frac{\text{lbmol VAc}}{\text{min} \cdot \text{lb catalyst}}\right]$$

and for R2:

$$r_2 = 1.9365 \cdot 10^5 e^{-10,116/T} \frac{p_{O_2} \left(1 + 0.68 p_{H_2O}\right)}{1 + 0.76 p_{O_2} \left(1 + 0.68 p_{H_2O}\right)} \left[\frac{\text{lbmol ethylene burned}}{\text{min} \cdot \text{lb catalyst}}\right]$$

In these expressions, T is absolute temperature in kelvins and p is the partial pressure of a component in psia. We also calculated the heat of reaction in the ideal gas standard state (25°C, 1 atm) by using available heats of formation of the components. The standard state heat of reaction is -42.1 kcal /mol of vinyl acetate for R1 and -316 kcal /mol of ethylene for R2. The reactions are thus quite exothermic, which we also observed in the laboratory.

Based on this information BCI is requesting that your company design a cost effective process to make 300 MM PPY of crude vinyl acetate. Since vinyl acetate and water form a heterogeneous azeotrope we refer to crude vinyl acetate as the acetic acid "free", liquid product which could be decanted off from the reaction water. The crude vinyl acetate will then contain water up to its solubility limit at say 20°C which is about 5 mol% water. The acetic acid in the crude vinyl acetate must be less than 0.1 mol%. BCI has existing columns on site capable of removing the remaining water, acetic acid and other byproducts from the crude vinyl acetate. We also suggest that you would use one of many standard principles (e.g. carbonate wash) for removing the byproduct carbon dioxide from the reaction mixture. In your flowsheet you need not design or analyze the carbon dioxide removal step in detail but simply assume that 99.5% of the carbon dioxide will be selectively removed from any stream sent to such a facility. The size (and cost) of the carbon dioxide removal unit will be proportional to the flow rate and composition of the stream sent to it. You may cost estimate the carbon dioxide removal unit as two packed towers (one absorber and one desorber) each with 30 equivalent stages. In the first tower, the absorber, CO_2 is absorbed in a cold liquid (assume water) containing a carbonate. In the second tower, the desorber, the CO_2 is liberated by reboiling the recirculating liquid. Based on our requirement that the desorber must operate at atmospheric pressure and that we would like to use cooling water for the absorption cooler, we have estimated the following heat load requirements for the CO_2 removal unit. This should aid you in estimating the diameter of the towers and the sizes of the heat exchangers depending on the nature of the stream you opt to purify.

Mol% Carbon Dioxide in the Vapor Stream Sent to the Absorption Tower	**Heating Requirement in the Desorption Tower and Cooling Requirement of the Recirculation Liquid [kcal/kmol Vapors Sent to Absorption]**
0.5	125
1	219
2	380
5	770
10	1,260
15	1,640

You may further assume that acetic acid is available from our tank farm as a liquid at 30°C. You may also assume that both ethylene and oxygen are available from separate gas headers at 200 psig and 30°C. The ethylene gas is 99.9% pure, the balance being ethane. The following utilities and services are available as needed at the battery limits. Costs are in 1996 dollars

150 psig steam	\$5/1,000 lb
50 psig stream	\$4/1,000 lb
Cooling tower water	\$0.09/1,000 gal
Raw water (makeup)	\$0.55/1,000 gal
-25°C Refrigeration	\$0.12/hr · ton
Electricity	\$0.065/kWhr

In designing the process we would like you to propose a design which minimizes the total product cost of crude vinyl acetate at the nominal rate of 300 MM PPY of pure vinyl acetate. Assume a 90% operating utility (7,884 hr/yr) and assume that 99% of the vinyl acetate in the crude stream can be recovered. The results we expect from your work include

- An optimized flowsheet
- Total installed equipment costs (onsite cost)

- A profitability analysis of the project
- A control scheme based on an in-depth operability analysis of the process

Physical properties for all components required in this study should be readily accessible from publicly available sources (e.g. DIPPR, HYSYS.Plant, etc.). This also pertains to mixture properties with the possible exception of the vinyl acetate (1)/water (2) binary. We therefore provide you with our best estimate of the VLE and LLE data for this pair.

VLE INFORMATION

CONSTANTS	A_{12}	A_{21}	α_{12}
van Laar	4.1549	2.1198	
Wilson	1,384.5959	2,266.3927	
NRTL	1,549	2,336	0.38

LLE INFORMATION

Solubility of water in vinyl acetate at 20°C : 4.949 mol%
Solubility of vinyl acetate in water at 20°C : 0.241 mol%

References

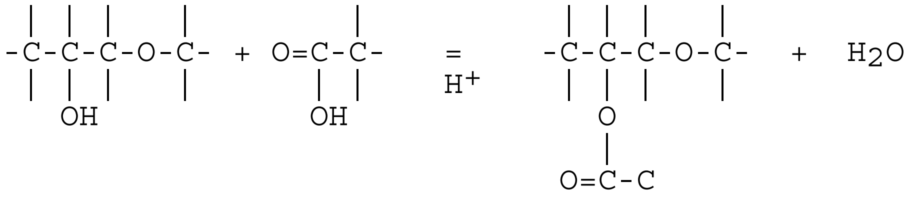
[1] Douglas, J.M., *Conceptual Design of Chemical Processes,* McGraw-Hill, 1988
[2] “Make Vinyl Acetate from Ethylene”, *Hydrocarbon Processing,* **46**, 4, 146-149 (1967)

A-IIS.1.12 PM Acetate Manufacture [PROC]
(Leonard A. Fabiano, ARCO Chemical, January 1993)

PM Acetate (propylene glycol mono-methyl-ether acetate) is a specialty solvent used in resins, coatings and cleaner formulations. Current sales volumes are 10 MM lb/yr and it is being produced batchwise by outside "tollers". Due to expected increases in demand, the PENNCO (your company's name) is interested in building its own continuous plant in the Houston area. The economic size must be determined that will yield a 15% after tax return while the sales build to 20 MM lb/yr in three years. Consider first a 20 MMlb/yr facility which will be integrated into an existing facility. Our R&D groups have developed a considerable amount of data on the process; i.e., chemical kinetics and VLE data. This information will be supplied after the design group signs a non-disclosure agreement with ARCO.

The primary chemistry is as follows:

PM Acetate Chemistry



PM HOAc PMA

Byproducts from Ether Cleavage

$$\text{PM} \begin{cases} + H_2O \xrightarrow{H^+} \text{PG} + \text{MeOH} \\ \xrightarrow{H^+} \text{allyl ether} + \text{MeOH} \end{cases}$$

$$\text{PG} + \text{HOAc} \longrightarrow \text{PG Acetate and PG Diacetate} + H_2O$$

$$\text{MeOH} + \text{HOAc} \longrightarrow \text{MeAc} + H_2O$$

where HOAc is acetic acid, PM is propylene glycol mono-methyl-ether, PG is propylene glycol, MeOH is methanol, and MeAc is methyl acetate.

Data have been developed on a boiling reactor concept that utilizes a liquid catalyst and a fixed-bed reactor concept that utilizes an acid resin catalyst. The fixed-bed option offers several advantages, in particular, in raw materials cost and handling, and in materials of construction. It is requested that you investigate the fixed-bed concept and compare it with a reactive distillation concept that utilizes the solid catalyst.

The expected market price, chemical kinetics and VLE data, and utility costs will be supplied at a later date. Where VLE data are lacking you may use the UNIFAC correlation. Your company has access to ASPEN PLUS which has a reactive distillation subroutine (RADFRAC).

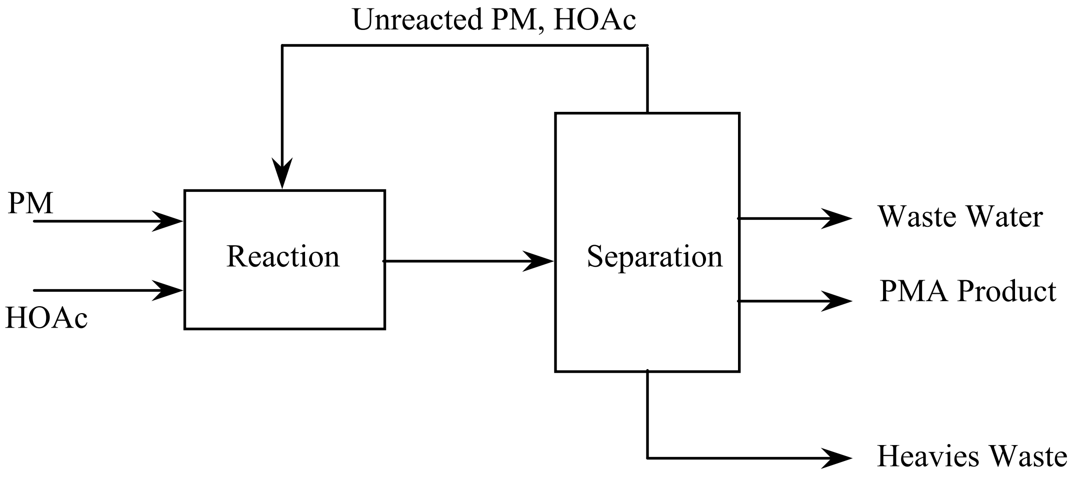
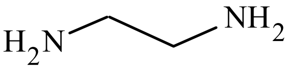


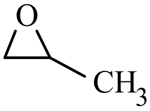
Figure A-IIS.3. Simplified Flowsheet for Fixed-bed Process

A-IIS.1.13 Propoxylated Ethylenediamine [PROC]
(Brian E. Farrell and David D. Brengel, Air Products and Chemicals, January 1994)

Ethylenediamine (EDA) is a versatile building block in the chemical industry for amine-based compounds.


EDA

A family of amine compounds can be formed from the reaction of EDA with propylene oxide (PO).


PO

Between 1 and 4 moles of PO can be added per mole of EDA. The monopropoxylated EDA can be used as an intermediate in the synthesis of a polyurethane catalyst. The di- and tri-propoxylates can be used as cross-linkers for epoxy systems. The fully propoxylated molecule is used as a cross-linker in polyurethane systems.

Your assignment, should you decide to accept it, is to synthesize and purify each of the EDA-PO reaction products. The required amount of each product will be determined according to market demand. IMF, the company that you work for, has performed extensive market research and will provide you with an estimate of market demand and selling price for each of the four compounds. The IMF research department has synthesized the four materials in small quantities and will make available their findings with regard to reaction kinetics and thermodynamics. You will be responsible for designing a reactor system and distillation process that best meets the anticipated market demands, while simultaneously maximizing IMF's profits.

A-IIS.1.14 Natural Gas to Liquids [PROC]

(William B. Retallick, Consultant, January 2005)

Despite the shortage of natural gas there are puddles of stranded gas that cannot get to market. This happens when the puddle is too far from a pipeline. Gas to liquid (GTL) is a process that is growing rapidly. The natural gas is partially oxidized to make syngas:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad (1)$$

And the syngas is reacted to make hydrocarbons:

$$nCO + 2nH_2 \rightarrow (CH_2)_n + nH_2O \qquad (2)$$

This is the Fischer-Tropsch reaction (1923). The original catalyst was iron; now it is cobalt. The long-chain hydrocarbon product $(CH_2)_n$ is hydrocracked to make useful products such as sulfur-free diesel fuel.

One way to make the syngas is to partially oxidize the natural gas on the surface of an oxygen ion conducting ceramic membrane. The membrane is potentially much cheaper than an air separation plant. The membrane is still in the development stage, and consequently, the cost is uncertain.

Your design team will design a gas to liquids plant with a membrane, and plot curves of membrane cost as a function of the cost of stranded gas, at constant rate(s) of return on investment, say 12%.

The design basis is:

1. The plant is located in Ohio.
2. The puddle of gas is one million SCFD, all methane, available at 300 psig.
3. The product is diesel fuel made by cracking the long chain product from the FT synthesis.
4. The rate of oxygen permeation through the membrane is the 0.128 $cm^3/cm^2 \cdot min$ (U. S. patents 6,488,739 and 6,544,404).

References

"Gas to Liquids", downloaded from www.Fischer-Tropsch.org.

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A-IIS.1.15 Retrofit of Isobutane Dehydrogenation Facility to make Propylene from Propane [PROC]

(Gary Sawyer, Lyondell, 2010)

In the late 1970s, ARCO Chemical developed a process to produce methyl tertiary butyl ether, MTBE, an excellent oxygen enhancer for gasoline. Over 30 large plants were constructed around the world to convert isobutylene and methanol to MTBE. Then in the late 1980s many large plants were shut down, many by state governments, due to the fear of its potential pollution of ground water. At this point, production is at about a third of its peak a few years ago, nearly all of which is exported to countries around the world. Also, in Europe, ethyl tertiary butyl ether, ETBE, is popular – as it is a renewable fuel from ethanol.

With many large-scale MTBE plants having been shut down, companies have been challenged to design processes for their existing equipment. Stated differently, companies are seeking to identify other chemicals that can be produced using much of their existing equipment. In short, these plants are being *retrofitted* to produce other chemicals. For this project, you are given a list of existing equipment items and asked to use them, with the addition of several new equipment items, in the design of a process to make propylene from propane. This is a timely problem, especially in the U.S., where few new grass-roots plants are being designed and built from scratch. Many engineering design teams are working on variations of this retrofit problem.

Because the current production of propylene from steam-cracker olefin units cannot keep up with the demand, this project is intended to investigate the possible retrofit of a butane dehydrogenation plant for propane dehydrogenation to propylene. As such, industry is continuing to bring significant amounts of propylene production capacity on-stream. You will determine the new equipment needed, and the limitations (“bottlenecks”) in the existing equipment.

A diagram of the process available for retrofit is shown in Figure 1. The part of the plant used to make MTBE from isobutylene (i.e., the MTBE unit) is not suitable for use in dehydrogenation. In addition, the cryogenic separation unit previously used to separate and purify hydrogen has been moved to another facility and you are asked to consider a new design for this part of the process. Note that this unit does not appear in Figure 1. Considerations can include:

Cryogenic separation
Pressure-swing adsorption
Temperature-swing adsorption
Membrane separations

The reaction is not completely selective to propylene. At the high temperatures needed, some side reactions include the generation of ethylene, methane, and coke; the latter is a carbon deposit on the catalyst. As the carbon deposits increase, the catalyst is deactivated and eventually, the reactor is taken off-line, purged, and regenerated with hot gas that is lean on oxygen to prevent overheating. The existing regeneration system regenerates one bed in 8 hours, at a cost of $100,000 per regeneration (mostly in utilities).

Propane dehydrogenation will require a “C3 Splitter” to separate and recycle unreacted propane. There are two grades of marketable propylene, polymer grade (99.5% propylene) and chemical grade (96% propylene). You must decide which grade to produce, or perhaps to produce some of each grade. Economics for the project are driven by the price difference between purchased propane at \$1.10/gallon and product propylene (45.5 ¢/lb chemical grade, 47 ¢/lb polymer grade). Also, what price would you have to pay for propane to achieve a target rate of return equal to 15%? Energy costs are \$7 per million Btu. Hydrogen co-product is priced at twice its heating value

A detailed equipment list, a spreadsheet available from W. D. Seider, is provided for the numbered items in Figure 1. Note that the design pressure is limited to 350 psig. You will need some equipment to remove ethylene from propylene. If you think the Depropanizer may be useful, details will be provided. There is no available refrigeration capacity at the site.

Catalysts for the reaction have been screened and the selected catalyst was tested in the laboratory to provide kinetic data. The experiments were done with a fixed amount of catalyst held at constant temperature in a “sand bath”. Pure propane was fed at various flow rates, and the exit concentrations of propylene and ethylene were measured with on-line spectroscopy. The results are in the spreadsheet available from W. D. Seider. Note that data was collected with catalyst of different “ages” or coke deposition. Also included is a “life study” of the catalyst to determine the rate of coking. The dehydrogenation reaction is reversible, and the mechanism is first-order in each component.

Propane ⇔ Propylene + Hydrogen

The decomposition reaction is irreversible, and first-order in propane:

Propane ➔ Ethylene + Methane

The coking reaction is not significant in its contribution to the gas-phase products, but it has a significant effect on the catalyst activity. The rate of the coking reaction is anticipated to be of the order *n* with respect to pressure; that is:

$$\frac{dC}{dt} = kP^{n} e^{\frac{E_a}{RT}}$$

where *C* is the amount of coke in wt% of virgin catalyst. The reaction is roughly:

Hydrocarbon (g) → Carbon (s) + Hydrogen (g)

The catalyst is ¼ inch extrudate with an average length of ¼ inch. The bulk density is 60 lb/ft^3 and catalyst costs \$15/lb with a 3-year life.

The data and equipment design is hypothetical for this problem. However, the propane and butane dehydrogenation processes are licensed and practiced. The Catofin® process from Lummus is similar in concept to what is shown in Figure A-IIS.4.

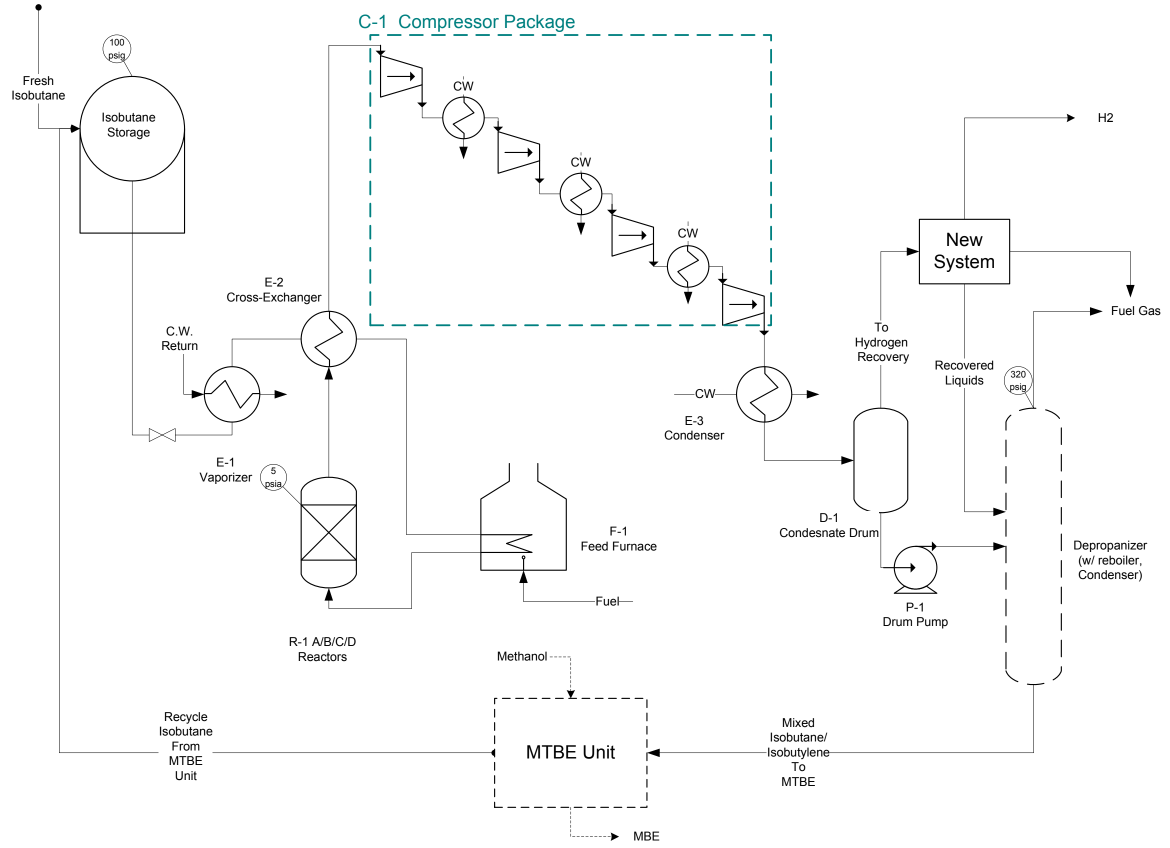
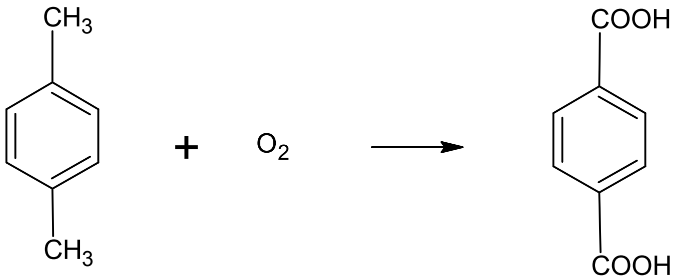


Figure A-IIS.4

A-IIS.1.16 Terephthalic Acid using Ionic Liquids [PROC]
(Bruce M. Vrana, DuPont, 2011)

The conventional route to terephthalic acid (TPA), one of the monomers for polyethylene terephthalate (PET), is over 50 years old and has not changed much since it was discovered by Scientific Design. PET is used in soda bottles, carpets, fibers, etc. Despite the huge growth in PET worldwide, essentially all TPA is produced by the Amoco process (now owned by BP) or similar processes. In the Amoco process, p-xylene (PX) is oxidized with air to TPA, in an acetic acid solvent. Capital costs are very high because of an extremely corrosive bromide catalyst promoter, which necessitates Hastelloy or other expensive alloys be used for the equipment.



SABIC has patented a novel catalyst system which is expected to solve the corrosion problem. They use an ionic liquid with an organic cation and bromide anion (1-ethyl-3-methylimidazolium bromide). PX conversion is 100%, selectivity to TPA is 95.6%, with similar byproducts formed as the Amoco process (p-toluic acid, 4-carboxybenzaldehyde, and 4-CBA).

4-CBA is a troublesome impurity in making purified terephthalic acid (PTA). Crude TPA made by this process must be purified by dissolving the product in water and reacting the 4-CBA away, as it is extremely difficult to separate from TPA. Crude TPA has 100 ppm of other impurities, but up to 2% 4-CBA.

Your company has asked your group to assess the technoeconomic feasibility of this ionic liquid discovery. You need to design a TPA plant through production of crude TPA using this new process. Purification to PTA is outside the scope of your effort.

Obviously, corrosion is a key uncertainty of the new route. Your company's chemists believe that the ionic liquid completely prevents bromide from leaching out and corroding the equipment. Analytical results confirm that belief, but long-term corrosion tests are currently being conducted in your labs. Management wants to proceed with your study in parallel with corrosion tests. Assuming the chemists' assertion is correct, you can use stainless steel for the process. Clearly, if that is not the case, then the process would have no advantage over the Amoco process and could not afford the expensive ionic liquid promoter.

Design a process to make 800MM lb/yr of TPA from PX at your plant complex on the U.S. Gulf Coast. PX is available on site for \$0.45/lb. Crude TPA is worth \$0.60/lb to your company. The ionic liquid promoter is estimated to cost \$25/lb when produced at the scale required to initially charge to your plant. All prices are forecasts by your marketing organization for long term average prices, expressed in 2011 at your plant site.

You will have to make many assumptions to complete your design, since the data you have is far from complete. State them explicitly in your report, so that management may understand the uncertainty in your design and economic projections before considering the next step toward commercialization – designing and running a pilot plant. Test your economics to reasonable ranges of your assumptions. If there are any possible "show-stoppers" (i.e., possible fatal flaws, if one assumption is incorrect that would make the design either technically infeasible or uneconomical), these need to be clearly communicated and understood before proceeding. Corrosion is one such show-stopper, but the question is whether there are any others.

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, if the plant is built, you will be there for the start-up and will have to live with whatever design decisions you have made.

Reference

European Patent 2,125,686, December 2, 2009, assigned to SABIC (equivalent to World Patent application 2008/074497, June 26, 2008)

A-IIS.1.17 Propane to Acrylic Acid [PROC]
(Bruce M. Vrana, DuPont, 2013)

Inexpensive natural gas in the U.S. from fracking is leading to a resurgence in the U.S. chemical industry and a wide array of new possibilities. Propane is now a low cost feedstock in the U.S., because it is produced as part of natural gas liquids from shale oil wells.

Acrylic acid is an important building block in the production of many industrial and consumer products. Most acrylic acid is consumed in polymer form, either directly or after synthesis of an acrylic ester. The esters are in turn consumed as co-monomers, which when polymerized are used in paints, textiles, coatings, adhesives and plastics. Acrylic acid is also polymerized to produce polyacrylic acid-based polymers that are used in superabsorbents, detergent, dispersants, flocculants and thickeners.

Until now, making an unsaturated acid from a saturated hydrocarbon has been elusive (except for butane to maleic anhydride). However, your company has developed a catalyst and one-step process to convert propane to acrylic acid in high yield. The vapor phase catalytic oxidation process has relatively low propane conversion per pass (by feeding an excess of propane compared to oxygen) to keep selectivity high. Propylene is also produced in the process, but can be recycled to the reactor for further reaction, ultimately to acrylic acid.

Your team has been assembled to develop a plant design to put this new catalyst into operation on the U.S. Gulf Coast. Management desires a plant to produce 200MM lb/yr of acrylic acid. They also desire a plant that uses this technology in the most economical way.

Propane is available by pipeline at your plant site for \$0.90/gal. Oxygen can be purchased for \$0.03/lb at 500 psig. Acrylic acid can be sold for \$1.75/lb. All prices are forecasts by your marketing organization for long-term average prices, expressed in 2013 dollars for the quantities needed delivered to your site or sold from your site.

You will need to make many assumptions to complete your design, since the data you have is far from complete. State them explicitly in your report, so that management may understand the uncertainty in your design and economic projections before approving an expensive pilot plant to provide the scale-up data you need to complete the design. Test your economics to reasonable ranges of your assumptions. If there are any possible "show-stoppers" (i.e., possible fatal flaws, if one assumption is incorrect that would make the design either technically infeasible or uneconomical), these need to be clearly communicated and understood before proceeding.

The plant design should be as environmentally friendly as possible, at a minimum meeting Federal and state emissions regulations. 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, if the plant is approved, you will be there for start-up and will have to live with whatever design decisions you have made.

Reference
U.S. Patent 8,193,387, June 5, 2012, assigned to Saudi Basic Industries Corp.

A-IIS.1.18 Propylene from Marcellus Shale Gas [PROC]

(John A. Wismer, Arkema, 2013)

The term "petrochemicals" is rapidly becoming a misnomer as ethylene – the primary base petrochemical – becomes increasingly derived from the ethane fraction of natural gas. The Marcellus Shale natural gas in Western Pennsylvania and West Virginia has become especially attractive to the petrochemical industry because it has an exceptionally high ethane content (about 15 wt%)). The North American market is actually more in need of propylene than ethylene. The east coast refineries have made by-product propylene readily available for years, causing it to sell at a discount to ethylene. As these refineries have been shutting down in recent years, the price relationship has reversed and propylene now sells at a premium to ethylene. Furthermore, of the two olefins, propylene's lower vapor pressure allows for much easier shipping by railcar.

This project envisions integrating pieces of known technology to make propylene from ethane derived ethylene. The plant would be situated in the western Marcellus shale region in the vicinity of a gas separations plant and a proposed world-scale ethylene plant. Existing rail infrastructure should enable this plant to supply both polypropylene plants on the East Coast or West Virginia. Plant capacity would be about 500 kT/yr.

The technology can be thought of as occurring in four steps: 1. ethane is converted to ethylene in a process known as steam cracking; 2. a portion of the ethylene is dimerized to butene-1; 3. butene-1 is isomerized to butene-2; 4. butene-2 is combined with ethylene in a methathesis reaction to form propylene. Normally, methasesis processes are designed to make a split of propylene and ethylene. However, one objective of this project will be to manipulate the recycle streams to convert the ethylene as completely as possible to propylene. Any heavies can be sold at gasoline value.

The conversion of ethane to ethylene by steam cracking is well known technology. In fact, Shell Petrochemicals is already exploring the possibility of a world-scale ethylene unit in Western Pennsylvania. A major problem for Shell is the lack of infrastructure in the region. They will require, among other things, the construction of underground salt domes for ethylene storage To take advantage of Shell's economies-of-scale and in turn reduce Shell's infrastructure burden, this project envisions a supply agreement with Shell by which ethylene is supplied by pipeline "over the fence" to the propylene facility. Since this will circumvent ethylene storage and transportation, it can be supplied at a substantial discount to market price. Supply contracts of this sort typically use some type of formula pricing. For shale-gas ethylene, the price would be scaled to the wellhead price of natural gas, combined with an inflation adjusted fixed cost and a capital recovery factor. Note that the wellhead price is usually about \$0.25/MMBtu less than the widely quoted NYMEX Henry Hub price. An example of this type of formula would be:

$$P = a(NG) + (FC)(i) + C$$

where P is the price of ethylene, typically in \$/lb; a is the usage factor for natural gas; NG is the price of natural gas, typically in \$/M; FC is the fixed cost per pound of ethylene in the base year; i is the inflation index; C is the capital recovery factor (designed to recover depreciation and fair return on both the ethane and ethylene plants). As part of the economic evaluation, you will need to understand enough about the ethylene manufacture to propose a fair pricing formula.

The propylene plant will first dimerize a portion of the ethylene to produce butene-1. Dimerization technology will be available by license as described in References 1 and 2. The undimerized ethylene will be a feedstock to the metatheses unit. The butene-1 needs to be converted to butene-2 to undergo metatheses. There are two approaches – one (Lummus) does the isomerization in-situ in the metathesis reactor[5] and the other (Axens-IFP) does it in a dedicated reactor[3]. The Lummus process is the only one practiced commercially but it is usually employed in shifting product mixes towards propylene, not complete conversion. The Lummus technology uses a high ethylene-to-butene ratio in the metathesis reactor to protect against the reaction of butene-1 and butene-2. The Axens process does the isomerization reaction external to the metathesis reactor. Although the conversion is less than complete, the butene isomers are somewhat separable by distillation (7°C boiling-point difference).

References

1. U.S. Patent 2011/0288308 A1, Nov. 24, 2011, "Process for Dimerization of Ethylene to Butene-1 using a …..", Grasset et al.

2. Alhumaizi, K.I., "Stability Analysis of the Ethylene Dimerization Reactor for the Selective Production of Butene-1", *Trans. IChemE*, **78**, Part A, April 2000.

3. U.S. Patent 2006/0161033 A1, July 20, 2006, "Production of Propylene Employing Dimerising Ethylene to 1-Butene, Hydroisomerization to 2-Butene, and Metathesis by Ethylene", Chodorge, J.A.

4. Gartside, R.J., and Greene, M.I., "Metathesis for Maximum Propylene", www.digitalrefining.com/article/1000078

5. U.S. Patent 2010/0056839 A1. Mar, 4, 2010, "Olefin Isomerization and Metathesis Catalyst", Ramachandran, B., et al.

6. Braziel, R., "Infrastructure Projects Connect Marcellus Shale to Ethane, NGL Markets", *The American Oil and Gas Reporter*, March 2011.

A-IIS.2 FUEL PRODUCTS (NON-RENEWABLE FUELS)

A-IIS.2.1 Fuel Additives for Cleaner Emissions [PROC]

(E. Robert Becker, Environex, January 1993)

Carbon monoxide and ozone levels are in excess of the National Ambient Air Quality Standards in the Northeastern states, which constitute a corridor from Virginia to New England. The principal source of carbon monoxide are emissions from automobiles. The coalition of Northeastern regulators have mandated cleaner burning fuels for the region; however, demand is uncertain since the member states can opt into the plan until 1995. The use of methyl-tert-butyl-ether (MTBE) as an octane enhancer provides significant reductions in carbon monoxide emissions.

Your company has technology for the production of MTBE. Your assignment is to provide management with a cost estimate for a 100,000 gallon per day MTBE plant in the Philadelphia tri-state area. Your report should estimate the product prices necessary for annual production rates of 100,000, 70,000, and 50,000 gallons. You have a stream of butane available from an adjoining refinery and you have to purchase methanol from a nearby chemical plant. Steam can be purchased from a cogenerator.

The process involves the dehydrogenation of isobutane to isobutene which is reacted with methanol to produce MTBE. Particular attention should be given to the dehydrogenation reactor design and operation. Technical and economic data for the design are attached.

Technical data

The rate of iso-butane dehydrogenation in kmol/kg cat-hr is:

$$\text{Rate} = k_r \frac{(p_a - p_e p_h / K}{(1 + 4p_h)^2}$$

where $k_r = 1.8\text{x } 10^7 \; e^{(-30{,}000/RT - 42c)}$

The rate of coke formation in kg carbon/kg catalyst-hr is:

$$\text{Rate} = k_c \frac{p_e}{(1 + 1.7 p_h^{0.5})^2}$$

where k_c = $5\text{x } 10^5 \; e^{(-21{,}000/RT - 45 \text{ x } c)}$

c = kg carbon per kg catalyst

p_a = partial pressure of isobutane [bar]

p_e = partial pressure of olefin [bar]
p_h = partial pressure of hydrogen [bar]
K = chemical equilibrium constant

The catalyst is 0.3 cm chromia alumina spheres with 0.48 void fraction and 1,200 kg/m^3 bulk density. The carbon is removed from the catalyst by burning in air at a rate of 0.1 kg carbon/kg catalyst-hr. The maximum catalyst temperature is 740˚C. The catalyst is replaced annually.

The reaction of isobutylene and methanol is assumed to go to 98% equilibrium without side reactions. The dehydrogenation reaction produces isobutene, hydrogen, propylene, and methane.

Cost and Economic Data

95% isobutane-5% *n*-butane is $ 0.70/gallon
Methanol is $0.75/gallon
Steam at 700˚C and 10 bar is available at $8.00/1,000 lb
Electricity cost is $ 0.07/kWhr
Fuel gas is valued at $2.00/MMBtu
Cooling water is $0.15/1,000 gal
Catalyst is $15/kg

Annual effective interest rate = 12% per year
Project life 10 years
Minimum investor's rate of return (IRR) is 15%

A-IIS.2.2 Liquid Fuels from Coal [PROC]

(William B. Retallick, Consultant, and E. Robert Becker, Environex, January 2005)

The U.S. has 27% of the world's coal reserves and only about 2% of its oil reserves; and consequently, the possibility of making liquid fuels from coal is very attractive. To accomplish this, coal can be gasified to generate syngas having the molar composition, CO and $2H_2$. Then, to generate liquid fuels, the Fischer-Tropsch reaction can be carried out:

$$nCO + 2nH_2 \rightarrow (CH_2)_n + nH_2O$$

In this project, a plant will be designed that generates syngas for a process to produce 50,000 barrels per day of liquid fuel; that is, about 0.3% of our daily petroleum consumption. Your syngas product must be ready to use; that is, at the proper pressure and purity. Note, however, that your design will not include the generation of liquid fuels.

Proximate analyses of coals from several mines in the U.S. are available. You should select a coal with high ash and low value, preferably from a strip mine. Your plant should be located at the mine, permitting the ash residue to be used to refill the mine.

Riegel's *Handbook of Industrial Chemistry*, 9th Edition, describes the gasification process. In your process, consider the use of two or more fluidized beds in series, fluidized with a mixture of steam and oxygen, which should permit the complete conversion of the carbon in the coal. Also, consider generating the oxygen by pressure-swing adsorption, although cryogenic and membrane separations from air might be attractive. Note that the book, *Fundamentals of Industrial Catalytic Processes*, by Bartholomew and Farrauto, describes the Fischer-Tropsch reaction – and provides information concerning the quality of the syngas required.

Your process should absorb heat to drive the gasification reaction, to heat the feed streams, to generate steam, etc. While heat can be provided by combustion:

$$C + O_2 \rightarrow CO_2 \quad ,$$

the CO_2 cannot be released to the atmosphere due to anticipated environmental regulations. Rather, it must be placed in the ground, preferably in an oil reservoir. For convenience, a CO_2 pipeline should be located nearby. Otherwise, the CO_2 would have to be liquefied and transported to the oil reservoir – at very high cost.

The following schematic, involving key economic parameters, is anticipated:

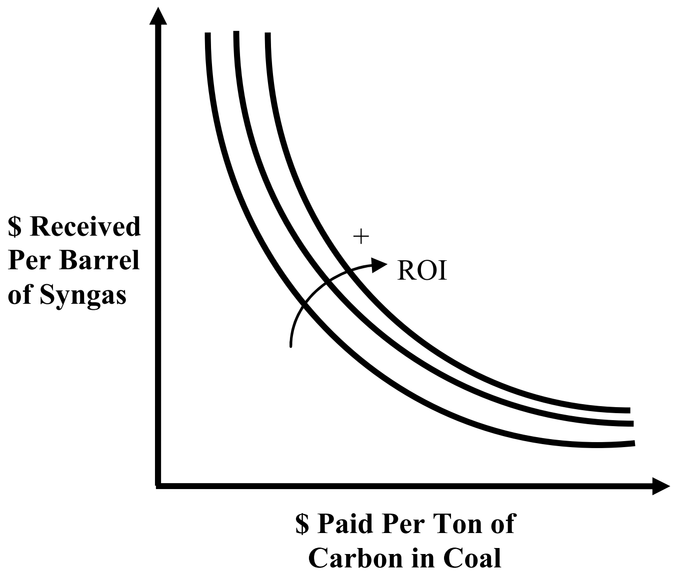


Figure A-IIS.5

Here, a "barrel of syngas" is defined as the amount of syngas needed to generate a barrel of the liquid product. Note that the ROI is the *return on investment*. For further details concerning the economic analysis, see the design report by Muth, Sales, and Rodriguez, *Natural Gas to Liquid Fuels Using Ion-transport Membrane Technology*, Univ. of Pennsylvania, SEAS Library, 2005.

References

Riegel's Handbook of Industrial Chemistry, 9^{th} Edition.

Bartholomew, C. H., and R. J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, 2^{nd} Edition, Wiley, 2006.

Muth, D., C. Sales, and E. Rodriguez, *Natural Gas to Liquid Fuels Using Ion-transport Membrane Technology*, U. Pennsylvania, SEAS Library, 2005.

A-IIS.2.3 Natural Gas Liquefaction using a CO_2-Precooled Reverse Brayton Cycle [PROC] (Adam A. Brostow, Air Products and Chemicals, 2009)

”Uncommon men require no common trust; give him but the scope and he will set the bounds.” -- Friedrich von Schiller

Introduction

Natural gas is a clean-burning fuel with high hydrogen to carbon ratio, a simpler alternative to hydrogen fuel. To transport natural gas from the well to the point of use, it is often liquefied and loaded onto a ship.

LNG (liquid natural gas) is typically prepared by the so-called propane-precooled mixed refrigerant (C3MR) cycle process. Natural gas is pre-cooled by vaporizing propane and liquefied by vaporizing a MR (mixed refrigerant), usually a mixture of hydrocarbons.

An FPSO (Floating Production, Storage and Offloading) is a type of plant that is mounted on a ship or an offshore platform. It can be moved from one location to another. There are two major issues in using the C3MR process in a shipboard application: sensitivity to the vessel motion and the fire hazard associated with the hydrocarbons, especially propane. While propane is volatile, it is sufficiently heavy for a flammable cloud to hover over the area for an extended period causing BLEVEs (Boiling Liquid Expanding Vapor Explosions).

An alternative to C3MR and other MR processes is the reverse-Brayton cycle and the CO_2-precooled reverse-Brayton cycle, typically using gaseous nitrogen as the refrigerant. These cycles are less efficient, but relatively simple, insensitive to motion, and potentially safer. They show promise for smaller plants build on solid ground, with many recent patents issued to various energy companies.

Background Information

In the figures that follow, several reverse-Brayton cycle configurations are shown, beginning with Figure 1, which shows the simplest possible implementation of the reverse-Brayton cycle. These are intended as introduction before the problem statement is presented in the next section.

In Figure A-IIS.6, gaseous refrigerant (e.g., nitrogen) is compressed in COMP, cooled to about-ambient temperature in an aftercooler, AC, further cooled in the liquefier-heat exchanger, HX, isentropically expanded in the expander (turbine), EXP, and warmed in the HX to provide refrigeration to liquefy natural gas. The heat exchanger, typically a brazed-aluminum core (BAHX) can be simulated using MHEATX in ASPEN PLUS.

Figure A-IIS.7 shows a *compander* (compressor-expander) and illustrates the power recycle (recovery) concept. Part of the refrigerant compression is done by compressor CMP directly driven by expander EXP.

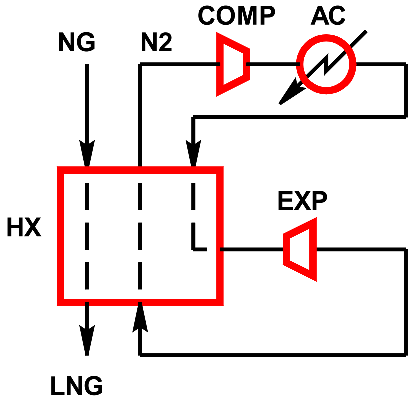


Figure A-IIS.6 Reverse-Brayton cycle

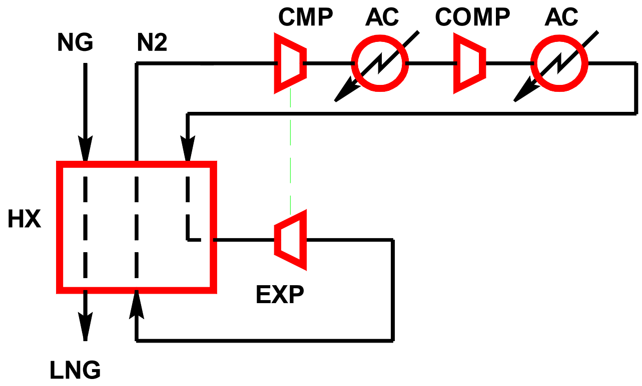


Figure A-IIS.7. Reverse-Brayton cycle with a compressor-expander

Figure A-IIS.8 shows a typical 2-expander liquefier. Two expanders, the warmer (EXP1) and colder (EXP2), improve the efficiency of the process. Optionally, they may drive two compressors: CMP1 and CMP2, providing a portion of the compression load.

Figure A-IIS.9 shows a precooled cycle, where additional refrigerant, such as propane (C3), is condensed, subcooled, throttled, and vaporized. Alternatively, the propane is replaced with CO_2, with multiple temperature levels of CO_2 used. Note that Figure 4 shows just one gaseous refrigerant expander, but two expanders can be used for better efficiency (as shown in Figure 3).

Is it necessary or economical to condense CO_2 prior to throttling? This is an important question to be answered by the design team, the answer to which is not obvious.

Environmentally friendly fluorinated hydrocarbons are alternatives to CO_2. While they don't deplete the ozone layer, they have a greater greenhouse effect than CO_2 and are difficult to generate offshore. Your design team is encouraged to investigate methods of producing CO_2 onsite to initially charge the system and to make up for seal losses.

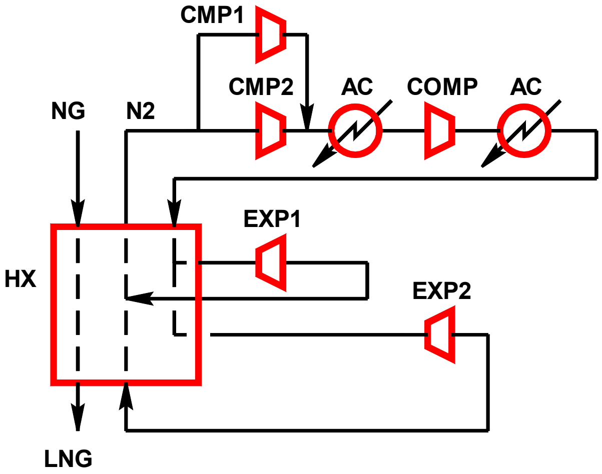


Figure A-IIS.8. Reverse-Brayton cycle with two expanders

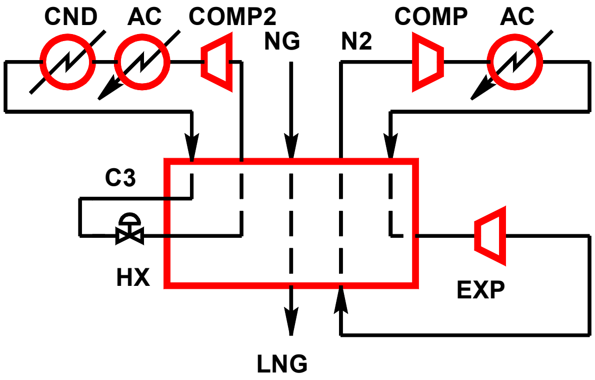


Figure A-IIS.9. Pre-cooled reverse-Brayton cycle.

Figure A-IIS.10 shows a liquefier with a scrub column. Here, natural gas is optionally expanded (to improve distillation), cooled in HX, and fed to the scrub column COL. The vapor overhead from the column is optionally recompressed, further cooled in HX, and fed to the phase separator, SEP. The liquid from SEP is used as reflux for COL. Vapor is liquefied to produce the LNG product.

The NGL (natural gas liquid) bottoms product is removed from COL to maintain the LNG heating value, to prevent heavier hydrocarbons from freezing during liquefaction, and to recover valuable products: ethane, LPG (light petroleum gas: propane and butane), and heavier components.

If time permits, the design team is encouraged to model a distillation sequence to recover C2, C3, and C4 in deethanizer, depropanizer, and debutanizer columns (not shown) and calculate the additional revenue from those products.

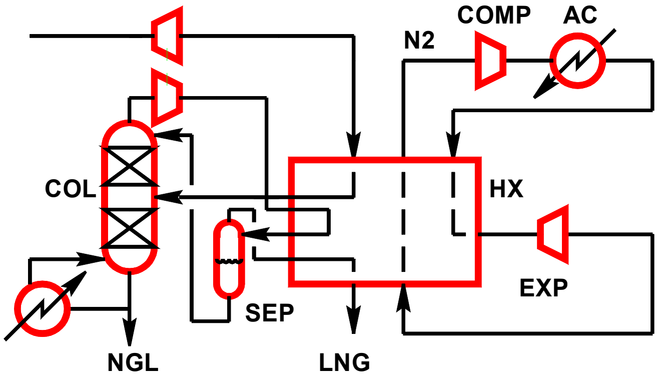


Figure A-IIS.10. Reverse-Brayton cycle with a scrub column

Figure A-IIS.11 shows a plant directly driven by a gas turbine (GT). Liquefied natural gas is throttled in a valve and fed to the product separator, PS. The LNG product is recovered from the bottom of the separator. Flash vapor from the separator is warmed in HX, compressed in fuel compressor, FC, and sent to the combustion chamber of the gas turbine, GT.

Air is compressed on the compressor side of the GT. It is then mixed with fuel in the combustion chamber, ignited, and expanded on the expander side to directly drive refrigerant compressor(s), CMP. As an alternative, the GT drives a generator while an electrical motor drives the compressor.

A new emerging technology is “aero derivative” turbines, which are based on jet engines – a more advanced technology.

Problem Statement

13,500 lbmole/hr of natural gas at 68^{o}F and at 725 psia containing 4% N_2, 87% C1 (methane), 5% C2 (ethane), 2% C3 (propane), 0.5% I4 (isobutane), 0.5% C4 (n-butane), 0.3% I5 (isopentane), 0.5% C5 (n-pentane), and 0.2% C6 (hexanes) is being liquefied. This roughly corresponds to 1 MTPA of LNG (1 million metric tons per annum).

The feed is cooled in a liquefier heat exchanger to a certain temperature (to be determined). It is then fed to the scrub column. The column overhead is further cooled in the liquefier heat exchanger. It is then fed to the reflux phase separator. Liquid from the reflux phase separator goes to the top of the column. Vapor from the reflux separator is cooled in the liquefier heat exchanger. The resulting fluid leaves the exchanger at about -230^{o}F. It is throttled to 18 psia in a product valve and fed to the LNG product separator.

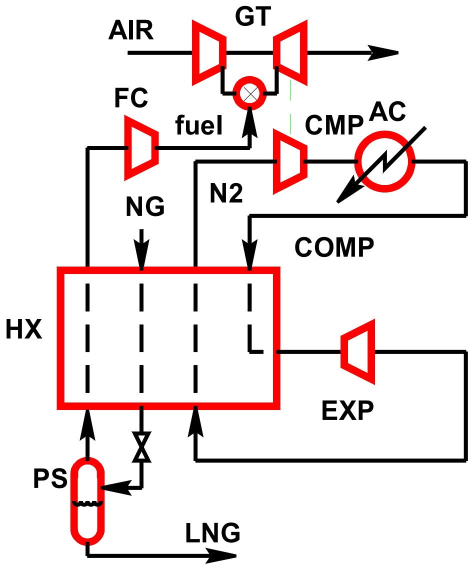


Figure A-IIS.11. Reverse-Brayton cycle with gas turbine

Liquid from the product separator is recovered as LNG product. Vapor is warmed in the liquefier heat exchanger, compressed to 500 psia, and fed to the combustion chamber of the gas turbine.

Vapor from the reflux phase separator cannot contain more than 0.1% C5+ (I5+C5+C6). Scrub column bottoms product should not contain more than 1% C1.

Column feed can be expanded to improve distillation; in that case the vapor is recompressed with power recovered from the feed expander.

The simplest refrigeration system to be considered is a single-expander nitrogen loop. Optimal process conditions are to be determined. Cooling water for the after-cooler is available at 68°F. Adiabatic (isentropic) efficiency of the compressor is 86% per stage. Adiabatic efficiency of the expander is 88%.

Another compressor driven by the expander is added to handle a portion of the compression load.

Then the second (warm) expander is added.

Finally, the CO_2 precooling loop is added (cooling water for the condenser is at 68°F). The design team is encouraged to find the best strategy to model the process step by step.

Another option is a single-expander system with precooling.

Depending on time available, the design team can model simpler and more complex systems and look at the capital-efficiency (specific power) tradeoff. Even a simple design is valuable as it may be economical for smaller plants. But at least one system should be precooled by at least one stage of CO_2.

The design team is to determine the limitations of using CO_2 as refrigerant and to determine whether it is necessary to condense CO_2 to achieve a working cycle. The team is also encouraged to find a way to generate CO_2 onsite.

Refrigerant compressor(s) are driven by an aero derivative gas turbine. Ambient air at 68°F and 14.7 psia is compressed to 500 psia (adiabatic efficiency of 78%). It is then mixed with fuel. The combustion temperature lies below 2350°F. The flue gas is expanded to about 8 inch Hg (adiabatic efficiency of 85%).

The design team is to model the gas turbine. The power requirement of the compressors determines the size and cost of the turbine. The fuel heating value determines the LNG temperature from the liquefier heat exchanger (initially assumed to be -230°F). In other words, the GT must satisfy both power demand and fuel balance.

If time permits, the design team can design a multiple-stage CO_2 precooling system and/or a ethane, propane, and butane recovery distillation system.

The plant economics data should be scaled to 0.5 MTPA and 2 MTPA to determine the impact of plant's size.

References

U.S. Patent 7,386,966 – describes CO_2-precooled LNG process with a condenser.

U.S. Patent 4,065,278 – describes conventional C3MR process with a scrub column.

Finn, A. J., "Effective LNG Production Offshore" – paper available from W. D. Seider

CO_2 P-H diagram – available from W. D. Seider

Air Products can provide some information about core sizing and costing. Much information is available online. The design team is encouraged to seek additional information and to modify/improve the process.

A-IIS.2.4 Alaskan Natural Gas to Liquid using Microchannel Reactors [PROC]
(John A. Wismer, Arkema, 2009)

The development of technology to convert methane to useful hydrocarbons has been escalating in recent years. This family of technologies – designated as Gas to Liquids or GTL – can target a variety of end products, such as methanol, gasoline or diesel fuel. As of today, most of the natural gas produced by oil wells in remote locations – sometimes referred to as stranded gas- is wasted. As a result, a premium is put on technologies most easily adapted to hostile environments. For most technologies the first step is the steam reforming of methane into a mixture of mostly CO and H_2 – usually called syngas. The syngas is then converted to a useful liquid, such as methanol, gasoline, or diesel fuel in a catalyzed synthesis reaction.

Your client is a major oil company that is exploring technology options in this area. You have been asked to evaluate a promising technology that offers the possibility of a compact plant through the use of microchannel technology. The use of microchannels in heat exchangers has been shown to increase overall heat transfer coefficients by as much as an order of magnitude. This technology has been extended to reactor systems, in which the combined effects of high heat and mass transfer rates yield very high reaction rates – even for highly exothermic or endothermic systems. The potentially small footprints of microchannel systems makes them ideally suited to the challenge of GTL processing in remote locations.

The proposed technology first proposes using the steam reforming of methane to produce a synthesis gas:

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$

In addition to being highly endothermic, the above reaction is both kinetically and equilibrium limited. Invariably, it is accompanied by the water-gas shift reaction.

$$CO + H_2O \leftrightarrow H_2 + CO_2$$

The required heat is often supplied by partial combustion of the methane using an air co feed. With the microchannel technology, the heat can be supplied by fuel combustion that occurs in adjacent channels[2,5]. Part of the advantage of microchannels is the ability to run combustion reactions in a controlled manner. The very high surface area to volume ratio allows free radicals to get "quenched" as they are formed, tempering the rate of combustion. Furthermore, since the heat of combustion is transferred as quickly as it is generated, there is no need to operate with a large amount of excess air in the combustion channels. On the process side, the channels are coated with a highly effective catalyst and diffusion is eliminated as a mass-transfer resistance.

The second step of the process is the Fischer-Tropsch synthesis, whereby the carbon monoxide in the syngas is hydrogenated into alipahatic hydrocarbons primarily. The target products are paraffinic oligomers in the C5 to C10 range:

$$(2n+1)\ H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$$

However, the synthesis also can produce olefins, alcohols, coke, and carbon dioxide[7]. The Fischer-Tropsch synthesis is highly exothermic. One of the non-selectives of Fischer-Tropsch synthesis is methane. Together with the light gases, methane can be recycled either to the inlet of the Fischer-Tropsch reactor or to the reformer.

One of the problems with the above process is that hydrogen is produced in excess. Either the excess hydrogen can be oxidized to recover energy or CO_2 from combustion can be added to the make up the carbon deficit. In most process concepts, the latter approach, called autothermal reforming[8], is used but that technique compromises some of the microchannel advantages. A major design challenge is to seek a heat and material balance that makes optimum use of the microchannel technology.

The only current commercialization venture involving this technology is an offshore oil drilling platform[6]. However, it appears to be well suited to onshore areas that place a premium on small footprint, low environmental-impact processing. The site for you to explore is the North Slope of Alaska, where this technology can be used in lieu of or as a stopgap measure for a trans-continental pipeline that is in the planning stages. In this sense, the North Slope gas is not truly stranded. BP claims that the pipeline project is more economical then GTL technologies at the gas production capacities of the North Slope[9]. However, the pipeline project is long term and expensive, costing $30B to $40B by the time it is completed in 2018, the earliest possible date. The scale of the GTL project should be about 100 kbpd – the scale originally proposed by Exxon for its now abandoned Alaskan GTL project[10]. At this capacity, the liquid product can be fed directly into the TAPS (Trans Alaskan Pipeline System) where it would be blended with crude oil for shipment to U.S. Northwest refineries. The current TAPS throughput is about 700kpd with a maximum capacity of about 2Mbpd. At this capacity, the TAPS will still have enough capacity to handle the ANWR oil – if it ever gets delivered.

References

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2. Cao, C. et al., "Catalyst Screening and Kinetic Studies Using Microchannel Reactors", Catalysis Today, **125**, 29-33 (2007).

3. Tonkovich et al., U.S. Patent 0033455A1, "Integrated combustion Reactors and Methods of Conducting Simultaneous Endothermic and Exothermic Reactions", Feb. 19, 2004

4. "A new Offshore GTL production System takes Advantage of Microchannel Reactors", *Chemical Engineering*, January, 2008.

5. www.pnl.gov/biobased/docs/**acs2003**presentation.pdf (Battelle presentation showing Fischer-Tropsch results).

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7. Alexander's Oil and Gas Connection, Voume 9, Issue #2- January 29,2004, "BP and Partner prove Alaska GTL technologies" at http://www.gasandoil.com/goc/company/cnn40481.htm

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A-IIS.2.5 Export of Marcellus Shale LNG [PROC]

(Ann Hewitt, Steven Lee, Ryan Marschang, and Tyler Moeller, 2014)

Overview

The Marcellus Shale natural gas field that spans from West Virginia to New York is leading the recent surge in domestic energy production, with the United States government predicting that the U.S. will be a liquefied natural gas (LNG) exporter by 2016.[1] This development has prompted the need for more LNG export facilities in the U.S. An inactive LNG import facility, Dominion Cove Point LNG in Maryland has the necessary infrastructure to transport natural gas from the Marcellus Shale and could be retrofitted to export LNG to locations around the world.[2]

Description

The Marcellus Shale field contains an estimated 177 trillion cubic feet of natural gas according to conservative estimates, with the actual total likely much higher. Companies continue to look for efficient, cost-effective ways of transferring this fuel to profitable locations, extending across the country and beyond. The most feasible option for transporting natural gas farther than 1,500 km is as LNG, which is created through a series of processes involving removal of water and contaminants, liquefaction, refrigeration, and storage before eventual transportation.[3]

The project involves designing an LNG facility to convert Marcellus Shale natural gas for export to global markets. Existing pipeline infrastructure is in place for a facility on the East Coast. Using materials and knowledge gained from the chemical engineering curriculum, the team will design a liquefaction process consisting of multiple stages, including pre-feed processing, liquefaction (refrigeration cycle), storage, product loading, and transportation. An efficient method of liquefaction to be considered is the Cascade process.[4]

A comparison of feasible LNG plant designs will be necessary. Floating LNG facilities are one alternative to traditional onshore plants. Another option is the retrofitting of the Dominion Cove Point LNG plant, which is currently set up to import but could be converted to an export facility. This project envisions an extensive analysis of the conversion from import to export, which will be considered along with an appropriate process design of gas liquefaction.

In addition to a strong technical foundation and design, this project will also investigate the economics of the various plant possibilities. Determining the costs to produce, liquefy, and transport the LNG will elucidate whether the cost to retrofit the Cove Point facility is feasible from a financial standpoint, beyond its technical merits. The economic advantage of converting the Cove Point facility is that the LNG tankage, port, and other infrastructure is already in place, likely resulting in a lower capital investment compared to building a new LNG export facility from scratch.

Furthermore, this project will inspect the economics of exporting Marcellus Shale gas. With the recent closure of the vast majority of nuclear power plants in Japan, the nation is more reliant now than ever before on imported natural gas to satisfy its energy needs. In 2012, United States natural gas (NG) prices were at 2.76 \$/MMBtu and Japan LNG prices were at 16.75 \$/ MMBtu in 2012, presenting a large U.S. economic opportunity for successful LNG production and export.[5] This project will present an economic analysis of a chemical process involving the costs of constructing and operating an LNG facility and distribution to a market where LNG is in high demand. The LNG markets in other countries are often locked into long-term contracts, unlike the natural gas market in the U.S., and this project will allow for the exploration of the current LNG financial landscape.

Key Points of Proposal

Design and construction of an LNG export plant based on a retrofit of an existing import facility with infrastructure to use Marcellus Shale gas as the feed.

Evaluation of different LNG processes/technologies with consideration for possible improvements and explanation of why converting an import facility into an export facility is cheaper than starting from scratch.

Evaluation of the economics involved in the decision to build an LNG plant.

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4. Verghese, J. and Ballout, N., “Development Options for North American LNG Export: The Merits of Inshore Deployed FLNG for Liquefaction of Onshore Shale Gas and Examination of Principal Technology Drivers.” *Offshore Technology Conference.* 2013. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=OTC-24091-MS&societyCode=OTC

A-IIS.3 GAS MANUFACTURE

A-IIS.3.1 Nitrogen Rejection Unit (from natural gas) [PROC]
(William B. Retallick, Consultant, January 2002)

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:

Flow rate, million SCFD	40	20
Pressure, psig	400	400
Helium, mol%	1.0	2.5
Nitrogen	16.0	28.0
Methane	balance	
Ethane	1.5	0.6
Propane	0.1	0.05
CO_2	0.01	0.00

1. Pipeline gas is to be delivered at 1,200 psig, containing no more than 2 mol% N_2.

2. Crude helium product contains at least 65 mol% helium, a maximum of 1 mol% methane, with the balance N_2, 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 ft^3 of helium content.

4. When heat is transferred (irreversibly) with a temperature difference, ΔT, the lost work is $Q\Delta T/T$, 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

Trautmann, S. R., and K. H. Janzen, "Innovative NRU Design at Pioneer Natural Resources' Fain Gas Plant.

A-IIS.3.2 Ultra-pure Nitrogen Generator [PROC]

(Jianguo Xu, Rakesh Agrawal, Mike Herron, Air Products and Chemicals, 2000)

As the semiconductor industry goes to submicron and deep submicron designs, the purity requirement for nitrogen gas is becoming higher and higher. The current specification for nitrogen requires the impurity levels to be below 10 parts per billion by volume.

Your company, UltraPureGas, is approached by a major semiconductor manufacturer (Advanced SemiCon) to submit a proposal to supply 200 ton/day of nitrogen at a pressure of 10 bar absolute to their megafab in Austin, Texas. The maximum allowable total impurities content (excluding noble gases such as argon, neon, and helium) is 10 parts per billion by volume. The customer also indicated that to avoid potential particulate contamination, nitrogen product compressors should be avoided. You, the lead process engineer for this project, are asked to come up with a low-cost design (which means you have to compare the different known processes and/or invent new processes and find the low-cost option).

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Venet, F. C., E. M. Dickson, and T. Nagamura, "Understand the Key Issues for High Purity Nitrogen Production", *Chem. Eng. Prog.*, p.78, January, 1993.

Wilson, K. B., A. R. Smith, and A. Theobald, "Air Purification for Cryogenic Air Separation Units", IOMA Broadcaster, January, 1984.

A-IIS.3.3 Nitrogen Production [PROC]
(Rakesh Agrawal, Air Products and Chemicals, January 1999)

Our Polymers Division needs a supply of moderately high purity nitrogen for its production applications. We would like to study the feasibility of incorporating new nitrogen plants with a minimum capacity of 5,000 SCFH (to handle current production) with the possibility of expansion to 40,000 SCFH. This plant is projected for 2005 when we expect the polymer market to expand significantly.

I am writing to you at this time to request a preliminary design for a nitrogen plant that produces 20,000 SCFH of polymerization grade nitrogen. In your design you will need to compute the price of nitrogen that yields an investors rate of return (IRR) of 15%. You should compare this calculated price with the price given in the Chemical Marketing Reporter.

Attached are relevant data on feedstocks, product specifications, utilities and economic data that should be useful for this design project. Additional data are also available in several articles in the library. For this production rate there are several competing technologies. To produce a competitive design, we would like to consider all of these technologies. These articles form only the start of your literature search. You will need to investigate potential ideas for this project thoroughly.

When preparing your design, you may also make the following assumptions:

1. Nitrogen product should be delivered as dry gas at ambient conditions
2. The plant should be designed for 8000 hours of operation per year
3. The product nitrogen should be at least 99% pure

Product Specifications

20,000 SCFH nitrogen gas

Minimum Nitrogen	99 vol %

Feedstock

Air at ambient conditions

Utilities

Cooling Water:

90°F supply temperature
115°F maximum return temperature

Steam System:

Saturated Steam from Offsite Boilers
Available at 150 and 600 psig

Process Water

Available at 90°F

Ambient Design Temperature:
100°F dry bulb, 90°F wet bulb

Economic Data

The following data are necessary for the economic evaluation. These include estimates needed for the 2005 analysis and follow trends over recent years.

1. Wage Rate	1998	2005
Labor ($/hr)	15.00	20.00
Supervision ($/hr)	25.00	30.00
Engineering ($/hr)	45.00	56.25

2. Utilities (Unit Costs)

	Unit	1998	2005
150 psig steam	1000 lb	3.31	4.00
600 psig steam	1000 lb	4.20	5.00
Fuel Oil (This is also the Fuel Value used for the purge)	106 Btu	2.02	2.50
Cooling Water	106 gal	68.10	70.00
Process Water	1000 gal	180.00	200.00
Electricity	1000 kWh	40.00	50.00
Steam Condensate	1000 gal	5.00	6.00
Inert Gas, low press.	1000 SCF	0.38	0.50

3. Waste Treatment

	Units	1996	2005
Hydraulic	$/yr/GPM	400.00	600.00
Organic	$/yr per lb/day	50.00	70.00

4. General Data

Payroll Charge	20 % of wages
Offsite, Utility Investment	40% of onsite investment
Repairs, Onsite	4%/yr of onsite investment
Repairs, Offsite	2%/yr of offsite investment
Supplies and Materials	2%/yr of onsite investment
Depreciation	8%/yr of total investment
Taxes, Insurance	3%/yr of total investment
Life of project	12 years
Income tax	32%
Minimum investors rate of return (IRR)	15%
Predicted Chemical Engineering Cost Index (2005)	400

Avoid steam systems. All compressors run on electricity rather than steam turbines.

References

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A-IIS.3.4 Krypton and Xenon from Air [PROC]
(Rakesh Agrawal and Brian E. Farrell, Air Products and Chemicals, 1991)

Krypton and Xenon are rare gases which are normally recovered from air. Recently, their demand has been on the rise. They are used in various applications - in several medical devices, long-lasting light bulbs, nuclear magnetic resonance, etc. The concentration of each of these gases in air is extremely low (below 5ppm). This makes their recovery from air challenging.

To produce reasonable quantities of krypton and xenon, both gases are recovered from large-tonnage plants for air separation that produce oxygen in quantities greater than 500 tons/day. These large plants are cryogenic in nature and operate at temperatures as low as -195˚C. Air is composed primarily of oxygen (20.95 mole %), nitrogen (78.12%) and argon (0.93%). However, besides argon, it has several contaminants such as hydrogen, helium, neon, carbon monoxide, methane and other hydrocarbons, water and carbon dioxide. Most of these contaminants are in much higher concentrations than krypton and xenon. The feed to the cryogenic air separation unit (ASU) is pressurized to about 6 atm before water, carbon dioxide and some hydrocarbons are adsorbed on molecular sieves. The air stream is cooled to near its dew point and distilled to recover nitrogen, argon and oxygen. Of these three constituents, nitrogen is the most volatile and oxygen the least. Contaminants such as hydrogen, helium, neon, and carbon monoxide concentrate at the top of the distillation column and leave with the nitrogen product. Krypton and xenon, along with methane, ethane, propane and some ethylene and propylene, are concentrated in the liquid oxygen (LOX) collected at the bottom of the distillation column. All of these components have boiling points higher than oxygen and are heavier. The efficient and economical recovery of krypton and xenon from LOX is the subject of this design project.

First, a conventional plant to recover krypton and xenon from the LOX will be designed. In this process, a portion of the LOX stream containing krypton, xenon and other hydrocarbons is withdrawn from the bottom of the main distillation column and passed through a bed to adsorb all the heavier hydrocarbons, including propylene and ethylene. None of the methane is adsorbed while some of ethane and propane are adsorbed. The LOX stream is fed to the top of the first distillation column to concentrate krypton and xenon (since the concentration in the feed LOX is below 50 ppm). However, the concentration of krypton and xenon in the bottom distillate from this column cannot be increased by more than a factor of about ten. The primary reason is that, along with krypton and xenon, hydrocarbons concentrate in the liquid phase. Concentrations of methane in liquid oxygen exceeding 50 ppm are unacceptable because they are explosive and present a safety hazard. The vapor from the top of this column is returned to the main distillation column and the liquid oxygen from the bottom, containing krypton, xenon, methane, ethane and propane, is vaporized in heat exchangers. The vaporized stream is heated to about 550˚C and sent to a catalytic unit to burn the hydrocarbons. The effluent from the catalytic unit is cooled and is passed through a molecular sieve adsorbent to remove the water and carbon dioxide formed during the reaction. The resulting stream is cooled to cryogenic temperatures, liquified and distilled to recover krypton and xenon. The oxygen stream from this distillation step is recycled to the first distillation column to recover krypton and xenon.

After the conventional process is designed, more recent technology will be considered. It may be possible to reject methane from the first distillation column and concentrate krypton and xenon by several orders of magnitude (as compared to a factor of about ten). Also, these processes can be made inherently safe by feeding nitrogen to the stripping section of a second distillation column, thereby displacing most of the oxygen from the krypton and xenon in the stripping section. Design of these processes should expose the opportunities for integrating the krypton/xenon distillation columns with heat and mass from the main air distillation units.

A-IIS.3.5 Ultra-High-Purity Oxygen [PROC]
(Mark R. Pillarella and Rakesh Agrawal, Air Products and Chemicals, January 1992)

Computers have revolutionized industry and technology over the past 15 years and can be expected to continue to do so. Improvements in computer technology are driven by improvements in semiconductor technology. For the production of high quality, defect-free semiconductors, ultra-high purity (UHP) oxygen is essential in the etching process. Typical cryogenic processes can produce oxygen with parts-per-million by volume impurities, but semiconductor manufacturing requires oxygen with impurities less than parts-per-billion by volume.

Your company, OxyPure, is submitting a proposal for a multi-million dollar contract to supply ultra-high purity oxygen to a major semiconductor manufacturer (SemiCon) in Southern California. OxyPure operates a conventional oxygen plant in Southern California which produces 400 metric tons per day of 1.3 bara standard grade gaseous oxygen (99.5% oxygen, 0.5% argon, 10 ppm methane, 0.5 ppm other hydrocarbons, 5 ppm krypton, 0.4 ppm xenon, 0.1 ppm nitrous oxide, essentially no nitrogen). The process flow diagram is shown in the Figure A-IIS.5. Your process engineering team has been assigned the task of evaluating several process schemes for modifying the existing plant to supply the semiconductor customer.

SemiCon requires 10-40 metric tons per day of 1.0 bara gaseous UHP oxygen. They have requested that proposals be submitted for two purity specifications;

(1) Less than 25 ppb of hydrocarbons; concentration levels of the other impurities acceptable.

(2) Less than 5 ppb argon and less than 5 ppb of the remaining impurities.

The process schemes to be evaluated are:

(A) Part of the standard grade oxygen can be reacted over a palladium or another suitable noble metal catalyst at 500°C, converting the hydrocarbons and some of the oxygen to carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The reactor effluent is passed through an adsorption bed (containing 5A or 13X molecular sieve adsorbent) to remove the CO_2 and H_2O (Giacobbe, 1989, 1991).

(B) Part of the standard grade oxygen can be fed to a standard three-component distillation process (requiring two additional distillation columns) to remove both the light and heavy impurities (King, 1980).

(C) A side stream can be withdrawn from the upper column and fed to an additional distillation column which removes the remaining impurities to produce UHP oxygen.

Develop each process scheme and compare the product purity, efficiency, and economics. Necessary process information will be supplied for the conventional oxygen plant.

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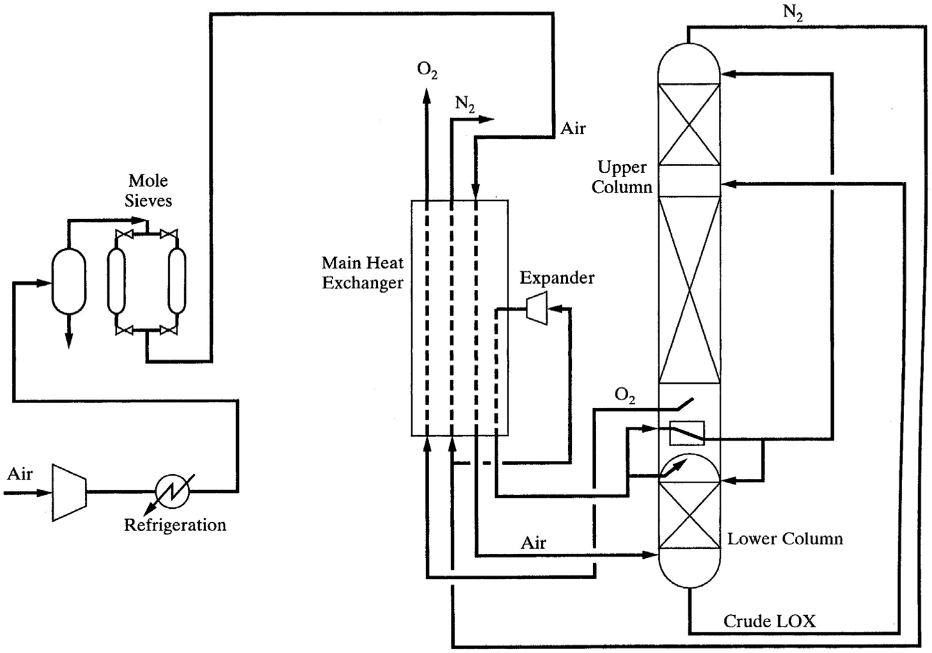

Figure A-IIS.12. A conventional process for oxygen production.

A-IIS.3.6 Autothermal Steam Reformer [PROC]

(William B. Retallick, Consultant, January 2003)

The Armed Forces need to generate electricity silently and with no tell-tale emissions. Fuel cells are the natural choice, with steam reformers needed to make hydrogen. The hydrocarbons to be steam reformed are the "logistic" fuels, diesel or jet fuel JP8. The reformers must be compact and have light weight. Your company, Catacel.com, has proposed a design wherein the reforming reactor and the heat exchanger are combined into a single module, which is the welded plate exchanger, made by Tranter, Inc. The plates of the exchanger are coated with combustion catalyst on one side and with reforming catalyst on the other side. Vaporized fuel and steam flow through the reforming channels while fuel and air flow through the combustion channels.

The Tranter publication shows the design of their exchanger. Catacel's reformer would comprise of a chain of exchangers connected in series. In each exchanger, the plates are 12 inches long and 4 inches wide. Spacing between the plates is 0.078 inches. Vaporized fuel for combustion is injected at the inlet of each combustor.

The water-gas shift section of the reactor follows the reforming section and is just a continuation of the reforming section. Cooling air instead of fuel plus air flows counter-current to the reformed products. This is shown in the patent application.

Following the shift section there is a membrane that separates pure hydrogen for the fuel cell. The shift output must be delivered to the membrane at a pressure of at least 10 psig. The residue gas that does not go through the membrane is incinerated. The heat release in the incinerator must be no more than 5% of the heating value in the incoming logistic fuel. The membrane and the incinerator are not included in your design. The output of the fuel cell is 100 kw. The efficiency of the fuel cell is about 50%, so that your reactor train must produce hydrogen at a rate of 6 kg/hr.

For the reforming reaction you will need some kinetic data. Herewith are data for reforming methane. You can assume that when the fuel is JP8 or diesel the catalyst will reform the same number of mols of carbon per second when the steam/carbon ratio is increased to 6. For the shift reaction, use the paper by Bunluesin, Gorte, and Graham. Assume that both catalysts and also the combustion catalyst can be coated onto the plates of the Tranter exchanger. For the combustion reaction, assume the limiting case wherein the reaction rate is limited by mass transfer. This is equivalent to assuming that every molecule that hits the geometric surface of the catalyst coating reacts immediately. Assume that the JP8 fuel has the properties of normal $C_{12}H_{26}$.

Your task is to minimize the weight of the chain of exchangers. Here is a way to do this:

1. Assume the number of plates in the exchangers, say 40.

2. Calculate the number of exchangers and the total weight. Also calculate the pressure drop.

3. Repeat with some other number of plates.

In making the calculations you have to keep the heat release on the combustion side of a plate in step with the heat absorbed on the reforming side.

References

Patent application titled “Autothermal Steam Reformer”.

Plot from the laboratory of Professor Greg Jackson at The University of Maryland, showing the activity of the reforming catalyst.

Paper by Bunlieson, Gorte, and Graham on the water-gas shift reaction.

Literature from Tranterphe, where phe is an abbreviation for plate heat exchangers

A-IIS.4 FOODS

A-IIS.4.1 Monosodium Glutamate [PROC]

(Robert M. Busche, Bio-en-gene-er Associates, January 1991)

In its efforts to expand into new specialty chemical markets, your company is considering manufacturing the flavor enhancer MSG (monosodium-L-glutamate monohydride) for the U.S. market by way of a joint venture with the Ajinomoto Company. Ajinomoto is the Japanese company that presently dominates the world market for MSG. The market situation in 1984 in millions of annual pounds was:

	Production	**Consumption**
S.E. Asia	397	300
Japan	191	175
Western Europe	106	105
South America	63	22
North America	0	73
Oceania	0	18
P.R. China and Others	110	174

With the help of Ajinomoto, the Marketing Department believes that it can capture a 50 million pound share of the North American market by the year 2000. Sales are expected to start at 20 million annual pounds in 1992; 30 in 1994; 41 in 1996; and 48 in 1998.

Presumably, the plant design will be based on the Ajinomoto batch fermentation process converted to a continuous mode using the aerobic bacterium *Brevibacterium ammoniagenes*. However, your Research Department recently was able to isolate a gene for a hemoglobin-like molecule from the aerobe *Vitreocilla* and express it in *Brevibacterium*. The recombinant cells contain hem and active hemoglobin. As a result, they appear to grow faster and to considerably higher cell densities than the conventional cells, especially when dissolved oxygen is less than 5% of air saturation.

Before committing to the joint venture, your president would like you, as Director of the Corporate Planning Department, to assess the expected economic performance of the Japanese process, as operated at your plant in Iowa and also to ascertain the sensitivity of the process economics to the use of the new organism.

The Japanese process operates with two fermenter stages. In the first stage, cells are grown to a density of 17.5 g/liter before inducing product expression. The cells are grown from glucose (corn syrup) according to the overall reaction:

$$C_6H_{12}O_6 + 3O_2 = 3CH_2O + 3CO_2 + 3H_2O$$

Six hours are allowed for growth.

The product is produced from the resting cells in the second stage, at pH 7.0-8.0, over a 28 hour period, at a concentration of 90 g/liter. The overall reaction to products is:

$$C_6H_{12}O_6 + 2.2065O_2 + 0.843NH_3 = 0.843\ C_5H_9O_4N + 1.785CO_2 + 3.471\ H_2O$$

Glucose conversion is essentially 100%. There is reason to believe that, with the new aerobe, production time might be reduced and cell density increased to, hopefully, 50 g/liter and, perhaps 100 g/liter. The allowable cell density will depend on viscosity restrictions to aeration performance of the new bacterium.

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A-IIS.4.2 Polysaccharides from Microalgae [PROC]

(Robert M. Busche, Bio-en-gene-er Associates, January 1986)

Research Department has discovered a way to produce polysaccharides (also known as water-soluble gums or biopolymers) from *Porphyridium cruentum*, a marine microalga. Process data are provided in the reference. The product is expected to find uses in existing food markets as a water-binding thickening agent, competing with such products as xanthan gum, agaur, alginates and carboxymethylcellulose. A very large potential new use is for enhanced oil recovery, where it can be used to increase the viscosity of sweep water relative to that of crude oil so as to promote the mobility of the residual oil in the reservoir. In this service, biopolymers are injected at a rate of 1.4 to 1.7 lb/barrel of oil recovered. Excluding the polymer, the cost of the polymer/sulfonate surfactant flood amounts to $30 to $40 per barrel of oil (including capital charges).

Your management has asked you to determine if the new product can be produced at a low enough cost to compete in the food and/or EOR markets.

Reference

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A-IIS.5 PHARMACEUTICALS

A-IIS.5.1 Generic Recombinant Human Tissue Plasminogen Activator (tPA) [PROC]

(Scott L. Diamond, University of Pennsylvania, January 2000)

***Setting*:**

Plasminogen activators are powerful enzymes that trigger the proteolytic degradation of blood clots that cause strokes and heart attacks. Genentech owns the patent for tPA, and currently sells 100 mg doses of recombinant tPA (activase) for about $2,000. The annual sales for tPA are about $300 MM/yr. However, the patent for tPA will be expiring soon. In response, Genentech has developed a next generation, FDA-approved, plasminogen activator called "TNK-tPA" which is slightly easier and safer for clinicians to use.

While a generic form of tPA may not compete well against TNK-tPA in the U.S., there may exist the opportunity to market a low-cost generic tPA in foreign markets where urokinase and streptokinase are low-cost (~$200/dose) alternatives that are associated with increased bleeding risks. Additionally, reduced healthcare reimbursements to U.S. hospitals may allow a generic tPA to compete against TNK-tPA or activase.

Process:

Produce recombinant tPA using CHO cells. Since Genentech will not license their CHO cells, your group will be responsible for cloning the human tPA gene and creating a stably expressing cell line for your process.

Constrants:

1) The product must be sold as a lyophilized, sterile powder (100 mg/bottle).

2) The product must be free of endotoxin contamination.

3) Affinity chromatography will be necessary.

4) Your separation system will operate as a batch system.

5) Your annual production will need to range from 30 to 100 kg/yr.

Determine:

1) Compare the cost of batch and CSTR (4 months per run) bioreactor operations.

2) Design a reverse osmosis/deionized water purification system to supply all process water.

3) Determine the steam requirements for sterilization of the bioreactors.

4) Does an economic opportunity exist for the production of generic tPA? Assume that Genentech is your only competitor.

5) Estimate the actual production cost per 100 mg/dose for Genentech to make tPA.

Assumptions:

1) Your reactor will use serum-free growth medium.

2) You have licensed the use of a hybridoma cell line that secretes tPA monoclonal antibody for the development of your affinity columns (life of column is 3 years). The license costs $120,000/yr.

Prerequisite:

The members of this design group must have completed ChE 479, *Intro. to Biotech. and Biochem. Eng*., or the equivalent.

A-IIS.5.2 Penicillin Manufacture [PROC]

(Robert M. Busche, Bio-en-gene-er Associates, January 1990)

Your large pharmaceutical company controls a major share of the worldwide penicillin market, which in 1985 reached about $600 million. However, your plants are relatively old and completely depreciated, with rising production costs. Management is alarmed that over recent years some market share has been lost to companies entering the market with new plants. A decision must be made as to whether to milk the present business as a cash cow without attempting to modernize (and without regard for further erosion of sales) or to build new facilities to replace the older plants while aggressively seeking to recapture the market share.

In the latter case, the Marketing Department forecasts that an additional 5 million pounds (about 3.6 billion units) of penicillin G potassium (potassium salt of benzyl penicillin acid) will be required by the year 2000; with 2 MM pounds by 1992; 3 MM by 1994; 4.1 MM by 1996; and 4.8 MM by 1998. Penicillin G potassium presently sells for about $18 per pound ($25 per billion units).

If a new plant is to be built, the design will be based on state-of-the-art technology using highly mutated strains of *Penicillium chrysogenum* growing on glucose (corn syrup). A conventional batch process will be used unless adaptation to a fed-batch or continuous process appears feasible. A crystalline product will be obtained after solvent extraction of the beer with amyl acetate or butyl acetate.

As Director of Engineering, you have been asked to design the plant, determine the investment required and assess the expected financial performance. You have also been asked to determine the cost-of-sales for the old plant at which it would no longer be competitive in profitability with a new plant.

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A-IIS.5.3 Novobiocin Manufacture [PROC]
(Robert M. Busche, Bio-en-gene-er Associates, January 1986)

Novobiocin is a general antibiotic produced by an aerobic fermentation of glucose by the organism *Streptomyces niveus*. The basic elements of the process appear to be the fermentation of *S. niveus* in an appropriate medium of substrate and minerals, the adsorption of Novobiocin (as well as other non-effective components expressed by the organism) on an ion exchange resin, and the desorption, concentration, and crystallization of a crude Novobiocin product consisting of 45% Novobiocin, 21% Isonovobiocin, and 34% other similar molecules.

The Research Director of your large pharmaceutical company is interested in initiating research on producing this product, but before committing funds, has asked you to evaluate the technoeconomic position the company might develop in this new business. From very preliminary studies, it appears that the amount of Novobiocin made per fermenter batch is small, and that much processing will have to be devoted to increasing yield and improving recovery efficiency. Also, as a result of low product concentration, oxygen transfer in the fermenter and power requirements appear critical to the design and cost.

Your Information Specialist has developed the following literature references to serve as the basis for your evaluation.

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A-IIS.5.4 Microfluidic Production of Depohalopendol with Controlled Release [PROC]

(John C. Crocker, Univ. Penn., Robert Meyer, Merck & Co., 2012)

Technology Overview: A common method for formulating drugs for long-duration time release ('depot') pharmaceuticals is to trap the active drug into polymer microspheres that are then suspended in water and injected intramuscularly. These spheres are small enough to fit down the bore of a hypodermic needle, and large enough to not get entrained into the blood circulation, typically 100 μm in diameter. The microspheres' matrix is formed of a PLA/PLGA (copoly lactic acid/glycolic acid) copolymer that decomposes by hydrolysis into products that are readily broken down by the body. This causes the matrix to become porous, allowing the drug payload to slowly diffuse out over the period of weeks. The current technology is based upon mechanically emulsifying a hydrophobic solution of a volatile solvent (dichloro-methane, DCM), drug and copolymer in an aqueous solution of poly vinyl alcohol (PVA) that both thickens the mixture and stabilizes the droplets against coalescence. This emulsion is then subjected to light vacuum, evaporating the DCM, 'drying' the PLA/PLGA/drug emulsions into drug-loaded solid polymer microspheres. This suspension can then be mixed with an adjuvant (e.g., a salt) to prevent particle aggregation and provide stability and isotonicity, and freeze dried to a storable powder. This mixture is then resuspended with water for injection directly prior to being injected into the patient.

The current technology has several challenges, mostly related to the broad size distribution of the mechanically emulsified particles. For one, very small particles release their payload almost immediately, creating a 'burst' of drug delivery at injection that presents an overdose hazard to the patient. For another, the clinically important release profile is itself a function of the size distribution, and to a lesser extent details of the drying process. Any variation in the size distribution created by the process leads to a corresponding variation in the release profile, which is clearly undesirable.

Project Statement: Numerous technologies for creating monodisperse emulsion droplets have been developed over the last few years, most based on some form of microfluidic technology. For this project, you will consider cross-flow membrane emulsification (XME), sketched in Figure A-IIS.13. In XME, an oily phase is driven through a small orifice in a rigid membrane into a cross-flow of an aqueous phase. The physical situation is akin to a dripping faucet on a windy day—an adherent drop forms on the orifice, which grows in size until the hydrodynamic stress of the cross-flow is high enough to tear the droplet off the orifice and downstream. A new drop then begins, and the process repeats itself. The dripping frequency, droplet size, and stable operating zone were analyzed in a recent publication [1]. The droplet size D is controlled by the density ρ, viscosity μ and shear rate (dv/dz) of the aqueous stream as well as the surface tension γ and orifice diameter D_0, while the dripping rate is controlled by the above as well as the oil flow rate Q_{DP}, up to a critical value where the system transitions to chaotic flow and jetting. This functionality is described in reference 1.

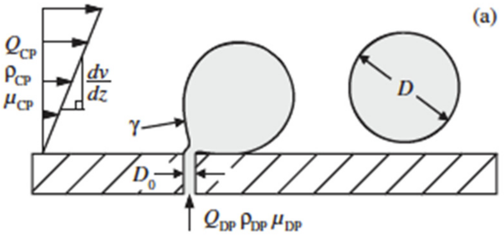

Figure A-IIS.13 A schematic of the cross-flow membrane emulsification (XME) process, with an oil drop growing while attached to a micropore orifice before eventually being torn away by a shear flow over the plate. Relevant variables are defined in the text.

Design Microfluidic Drop Formation Device

XME has also been used to produce drug-loaded PLA/PLGA microspheres, described in recent publications [2, 3]. The particles produced were highly monodisperse, presumably resulting in a highly controlled and reproducible release profile [4]. A nice feature of this technology is that it is readily parallelizable—throughput can be increased by drilling multiple orifices in the same membrane, located in the floor of a channel carrying the aqueous phase. In principle, the droplet/particle size from each orifice will be determined by the shear rate of the flow over it. This allows the overall droplet/particle size distribution to be readily engineered by spatially varying the shear rate in different parts of the channel and the distribution of pores in the channel floor.

One part of the project is to design the XME-based process equipment needed to produce a generic anti-psychotic medication (haloperidol) in a depot formulation at a commercially relevant scale of 10 million patient doses/yr. It is assumed that this process will be performed within the confines of a pharmaceutical manufacturing facility and will adhere to appropriate quality control standards defined by the United States Pharmacopeia and 21CFR parts 210 and 211, also known as good manufacturing practices. This process should be designed to be continuous or batch-continuous. Capital and operating costs for the process should be estimated based on current literature.

Model Drug Release Profiles

The second part of the design project is to model and engineer the release profiles from a given microparticle size distribution, based upon typical particle size-dependent release profiles that are available in the literature [5]. Several parts will be considered. (*i*) numerically solving a one-dimensional (spherically symmetric) differential equation for the release process to fit the literature results (*ii*) performance of an optimization to design a particle size distribution that most closely yields a constant release profile (a linear cumulant released dose curve) and (*iii*) performing a channel shape and orifice layout design that yields the desired particle-size distribution, likely requiring three-dimensional computational fluid dynamics simulations at small Reynolds number.

References

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A-IIS.5.5 Non-Egg-Based Flu Vaccine [PROC]

(Tiffany D. Rau, Eli Lilly, 2012)

Overview: Create a development program and pilot-plant facility for the production of flu vaccine using a production system other than eggs. The process developed, and the manufacturing facility to be designed eventually (not by your design group), must be able to respond to a pandemic.

Description

You are part of a world-leading vaccine company and you are in charge of creating a new platform within your company to manufacture vaccines. You will be concentrating on flu vaccine for this project, but once you obtain proof-of-concept, your platform will be considered for current and future products beyond flu vaccine.

Historically your company has produced vaccines in chicken eggs and this has been the production method for years, but it has benefits and risks. Some of the benefits are that the egg-based platform is well-documented and is approved worldwide. The egg-based platform also has allowed the company to quickly develop a new vaccine every year for the market as the strains differ each year and also deliver it to patients within a short timeframe. There are risks with an egg-based platform and one of the risks is that the egg supply may become unavailable due to a bird flu outbreak, for example. Note that duck eggs are often considered safer to use than chicken eggs because ducks are less susceptible to disease compared to chickens, but they also have drawbacks. Also note that many people cannot take the vaccine due to their allergies to eggs and feathers, which limits the population that can benefit from it. There are also scalability challenges requiring more eggs as the need for vaccine increases – and many other reasons having platform options will prove beneficial as the company's portfolio not only provides flu vaccines.

It is suggested that you use either a mammalian cell-culture system or a bacterial system for your new process, because your sister company has much experience with both types of organisms, enabling you to use them as an additional knowledge resource. The vaccine made using the alternative non-egg based process will have the same potency as that from the egg-based process; i.e., you will need the same concentration of vaccine per patient. You will be focused on delivering vaccine to both the North American and European markets. Also the quantity of doses that you will need to manufacture will be based on historical data; e.g., the number of doses Sanofi Pasteur or GlaxoSmithKline produce for the market.

Once you decide on the new vaccine production organism and process, you will design the pilot-scale facility – sufficiently large to produce enough product to perform proof-of-concept studies as well as for TOX studies. Please note that the commercial production facility will be used every year to produce the flu vaccine, but will not be used year-round because flu vaccine is a "seasonal" product. Also, until other products become part of your company's portfolio, this will be a single-product facility. Keep in mind that you have options such as the following for a commercial manufacturing facility:

1. A traditional steam-in-place (SIP) and clean-in-place (CIP) production facility on the company site or at a contract manufacturer (CMO).

2. A traditional production facility using some disposable technologies such as disposable mixing vessels (e.g., Allegro™ by Pall) or bioreactors on the company site or at a CMO.

3. A non-traditional facility with almost all steps of the process using disposables; i.e., a version of the Flex Factory on the company site or at a CMO.

There is a movement in industry to use disposables in manufacturing facilities, especially in contract development and manufacturing facilities – because there are no CIP or SIP protocols. Also, the vessels arrive sterilized and validated from the manufacturers – therefore, no extensive validation protocols are needed. Less initial capital is typically required for a facility that uses disposable technologies.

Your pilot plant and manufacturing facilities will include everything from vial thaw to purification, but final formulation and packaging will take place offsite and should only be mentioned in your report. On completion of this project, you will have selected the organism, and designed the process and pilot plant. You will also have discussed the production facility to make the next generation of flu vaccine for your company, but you will not have designed it. A diverse team of engineers, scientists, regulatory experts, as well as business leaders, has been established to help you deliver on your project. Your project is on the critical path and your patients are waiting.

Helpful/Interesting Information

Examples of vaccine manufacturers: GlaxoSmithKline, Merck, Novartis, Sanofi-Pasteur and many more.

You may find the Biopharmaceutical SUPERPRO DESIGNER model example on Intelligen's website www.intelligen.com is helpful as you create your design project. Please note that the model works using their evaluation version which is downloadable on their website. The evaluation version of the software does not allow the user to print or save files.

The FDA has given suggested guidelines for the internal layout of a biopharmaceutical facility/vaccine facility. You may wish to refer to their website for guidance: http://www.fda.gov.

Industrial trade publications: *BioPharm International*, *BioProcess International*, *Pharmaceutical Manufacturing*, *Genetic and Engineering News* (*GEN*), and many more.

Biotechnology Consultants: http://www.bptc.com. This is a consulting group that has posted several presentations you may find useful.

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Note: The creator of this project is not based in Philadelphia. Consequently, many if not all interactions with the student design group will be using SKYPE, phone and/or email. When selecting this problem, please take this into consideration as interactions will be remote. Please note that this is not unusual – as interactions involving the latest technologies often have a virtual presence. The creator has delivered projects all over the world without being present onsite.

A-IIS.6 BIOMEDICAL

A-IIS.6.1 Screening of Kinase Inhibitors using Microfluidics [PROD]

(John C. Crocker, University of Pennsylvania, January 2005)

A promising class of cancer therapeutics are kinase inhibitors (KIs), small molecule compounds that reduce the phosphorylation activity of one or more of the ~500 kinase enzymes in the human body (examples include gleevec, temserolimus, gefitinib, staurosporine...). To be useful, a KI must be specific—targeting one or a small number of kinases, without significantly affecting the activity of the others. It has been estimated that pharmaceutical companies are currently spending ~\$300MM/year screening potential therapeutic KI compounds created by their drug discovery efforts.

This project is to design a 'small start-up' scale facility to perform standardized kinase inhibition assays on compounds sent from pharmaceutical companies with reasonable turn-around time (a few business days). Target plant capacity should be about 10^4 assays per day at a market price of \$2 per one compound/one kinase assay. This leads to about 2.5MM assays/yr and \$5MM/yr revenue (assuming reasonable downtime). All reagents can be purchased commercially or easily synthesized in house using bench-scale equipment. The high cost of the purified kinases (typically \$5MM/gram) requires the use of at most 10-100 nanoliter total reaction volume per assay. The small revenue stream precludes a high-capital, brute force approach to achieving the necessary throughput. Instead, the reagents and samples will need to be handled and mixed using microfluidic methods, such as pen spotter or inkjet techniques. Ideally kinase function and reactant concentration will be followed in real time using non-destructive, non-contact methods such as fluorescence depolarization photometry (FDP), fluorescent resonant energy transfer (FRET) or luminescence, which can be readily parallelized so that a single CCD detector/scanner can monitor several hundred or thousand assays in parallel.

In general, each kinase is a protein which phosphorylates a specific protein or set of proteins, affecting their function much like an on/off switch. Along with phosphatases that remove phosphate groups, these enzymes are largely responsible for the biochemical regulation within living cells. In general, the reaction resembles:

$$\text{kinase} + \text{target} + \text{ATP} \rightarrow \text{kinase} + (\text{target})\text{PO}_4 + \text{ADP}$$

That is, the kinase binds adenosine triphosphate (ATP) and an active site on a target protein, moves one phosphate group onto the target and unbinds, releasing the target and ADP. As an enzyme, the kinase is not modified and repeats the reaction as long as target protein and ATP are available. Roughly 80 kinases have been cloned to date and may be considered commercially available for the purposes of this project. Rather than obtaining purified versions of all the target proteins as well, you should assume that a short peptide exists that can reliably mimic the target's active site, and which is small enough to be synthesized on site using a standard polypeptide synthesis unit. The function of the KI is to compete with the target by binding to the kinase's active site. When binding is strong, it effectively blocks access to the target protein and significantly slows the above reaction. Your companies' product consists essentially of inhibition concentration 50% (IC_{50}) data: the KI concentration at which a given kinase's activity drops by 50% (or reasonable bounds on IC_{50} in the case that inhibition is unexpected/undesirable). This is traditionally determined by performing multiple assays varying KI concentration over many orders of magnitude, and finding the cross-over (if any) in the resulting "S"-shaped inhibition curve. For example, a simple approach would be to use luminescence to report the concentration of ATP. Firefly luciferase and similar compounds produce light using an ATP dependent chemical reaction; the brightness of the light is essentially proportional to [ATP]. Thus, a low-light CCD camera could integrate the light signal for a short period, and the brightness of a few pixels would be proportional to [ATP]. The time rate of change of [ATP] would then be proportional to the consumption of ATP by the kinase (assuming that the amount consumed by the luciferase was negligible by comparison).

A major goal is this project is to design and evaluate methods for performing such an IC_{50} assay cheaply enough to produce a profit at $2 per "S" curve. The simplest (baseline) approach is to simply scale-down the tradional assay: use inkjet printing technology to mix the reagents together in small, separate droplets on a flat plate, with 10-15 droplets per KI, each having graded dilutions of the KI. In principle, one CCD camera could read the luminescence from thousands of such droplets simultaneously, making (perhaps) for a cost effective approach.

We are also interested in your designing a microfluidic apparatus that obtains the entire inhibition curve at once. The current "standard" approach for building microfluidic devices is to mold them from a silicone rubber, polydimethyl siloxane (PDMS). The resulting devices can range from simple networks of tubes, to densely integrated multi-layer fluidic devices, such as those manufactured by *Fluidigm* and *Agilent*. For low-cost screening of IC_{50}, you should consider very simple devices that use capillary forces and diffusion to passively fill a simple network of tubes and reservoirs. For example, a branched capillary network attached to KI reservoirs and sinks can set up (via diffusion) a steady-state gradient of KI concentration spanning many orders of magnitude. If the kinase, peptide and ATP are distributed uniformly, IC_{50} can be inferred from the position in the network at which the signal (e.g. rate of change in luminescence) drops by 50%. In a second possible design, if the KI diffused slowly into a prefilled kinase/peptide/ATP reservoir, one could determine the time at which kinase activity dropped to 50%, and infer the corresponding KI concentration. The central question is whether the microfluidic device will save enough reagent costs relative to its manufacturing costs to beat the baseline strategy above (which has no microfluidic network). In most cases, the devices' behavior should be amenable to a simple, lumped-element approach using ODEs, while more complex designs may require numerical PDE modeling (e.g., using FEMLAB).

Tailoring the screening process to your client's needs has the potential to increase profitability. For example, if most potential KI's have at least one undesirable inhibition of a non-targeted kinase, then the customer is primarily interested in ruling out compounds for further study. In this case, it might be cheaper (e.g., more profitable) to do a simple screen for inhibition at high KI concentration, and then only perform the full IC_{50} measurements for all 80 kinases for those rare compounds that pass the initial screen.

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Caliper Life Sciences:
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Promega (Kinase-Glo luminescence assay):
http://www.promega.com/kinaseglo/
Alpha Innotech (scanners): http://www.alphainnotech.com/productfiles/prodoverview.asp

A-IIS.6.2 PlasmaFluor Microfluidic Blood Coagulation Analyzer [PROD]
(John C. Crocker, University of Pennsylvania, January 2006)

The process of blood clotting in response to injury is a remarkably complex chemical process involving the rapid polymerization of fibrin filaments from monomeric fibrinogen precursors via the enzymatic activity of thrombin. The production of thrombin from its precursor prothrombin is regulated by numerous clotting factors and auxiliary proteins, resulting in thrombin's essentially autocatalytic production at an injury site. Abnormalities of this 'coagulation cascade' reaction can lead to uncontrolled bleeding or, in the other extreme, undesirable clotting within the bloodstream; that is, thrombosis. Laboratory screening for common clotting abnormalities is frequently performed prior to elective surgical procedures, and additional screens for abnormal clotting function are performed periodically on those patients in post-surgical recovery, with major infections or receiving anti-thrombosis therapy (e.g., with heparin). While some clotting tests can be performed in a hospital laboratory in as little as 10 minutes using semi-automated 'coagulation analyzers', these results are unavailable to patients in an ambulance or may be too slow for a patient in the middle of surgery. This project is to design a miniaturized, fully automated, high-speed coagulation analyzer suitable for use in operating rooms, trauma centers and ambulances.

Existing coagulation analyzers are bench-top units with internal robotic fluid handling systems, reagent and buffer storage, heating and refrigeration systems, integrated centrifuges for blood separation, and optical sensors for reading out sample turbidity, color, or scattering properties, depending upon which assay is being performed. One common class of assays is performed on a blood sample in which coagulation has been suppressed by chelation of calcium ions (e.g., by using EDTA). The plasma fraction is physically separated, reagents and calcium are added to it to initiate the coagulation cascade, which is then generally monitored by turbidity of the sample. The time to the first significant change in turbidity is termed the prothrombin time (PT), which is typically of order 10 seconds. Many other assays are based upon changes to this measure of clotting speed in response to added cofactors, termed the Activated Partial Thromboplastin Time (APTT). One particularly important clotting assay detects insensitivity to a clotting co-factor called 'protein C'. Activated Protein C Resistance (APCR) is highly correlated with the development of deep vein thrombosis (DVT), which is commonly (~20% of cases) caused by a familial mutation for clotting Factor V (FV). Obviously, diagnosis of APCR is especially important in patients undergoing major surgery or who have suffered a traumatic injury.

Your designed miniaturized analyzer should determine diagnostically reliable PT, APTT and APCR data in at most 5 and preferably less than 2 minutes. It should be small and rugged enough to operate in a crowded ER or ambulance, but need not be hand-held. For a baseline design assumption, your team may assume that the instrument will consist of two parts, resembling an inkjet printer and its disposable ink cartridges. Like the printer, the 'analyzer' component will contain the fully reusable systems including power, temperature control, user interface, optical sources and detectors, and computing hardware for real-time analysis. Like an ink cartridge, the analyzer 'cartridge' will be disposable, easily swappable and contain all the reagents and microfluidic handling systems on a 'lab-on-a-chip', along the lines of the recently developed microfluidic platforms by Agilent or Fluidigm. Details regarding blood sampling and the patient interface are largely outside this project, as it can be assumed that the medically trained user will be familiar with blood drawing techniques, and will inject a small sample directly into the cartridge. Production costs for the reusable analyzer should be less than $20K at expected production volume, and per patient/per sample disposable cartridges should be priced at $100/unit or below. Economic and market size analysis should be performed on both the production of analyzers and disposables, but it is expected that the primary source of revenue will be the latter. The analyzers may be sold near or below cost.

Coagulation assays are complicated multi-component reactions with non-linear kinetics, based on mixtures of costly, highly purified natural protein products, sera, synthetic reagents, and whole blood containing intact cells. The team can assume that all reagents are commercially available from existing coagulation analyzer manufacturers and reagent suppliers. Literature from those suppliers will provide useful information about reagent prices, storability, assay chemistry, and diagnostic utility.

A significant portion of this design project is to determine the best approach to realizing the above stated goals by the careful consideration of multiple alternative designs. The selection of the final implementation is up to the team and their advisor; design alternatives and selection criteria should be fully described in the final report. Design of the reusable instrument need not contain detailed component layouts, and may consist of component specifications and vendors as well as mass, volume, power and cost budgeting adequate to assess overall design feasibility and marketability. Detailed layouts, process flow diagrams, and engineering analyses of the microfluidic systems is expected. While the engineering approach to the design is unspecified, key design criteria are described below.

A major design challenge is storability, as many reactants have short shelf-lives (< 1day) at ambient temperatures. One approach is to preload all required reactants into closed reservoirs on the microfluidic cartridge and to store the entire cartridges at 4°C (refrigerator/ice chest) in their hermetic packaging until use. While lower temperatures, such as –20°C (standard freezer) will extend the shelf-life of many reagents, many protein products can not be frozen without loss of activity. A minimum shelf-life of 45 days (at a specified storage temperature) should be an assumed goal, to allow for reasonable inventory procedures (at the manufacturer and user sites) and express shipping. If needed, protein reagents that unduly limit shelf-life may be lyophilized (freeze-dried) for long term storability, but the microfluidic system must then contain on-chip units for rapid reconstitution of the powder reagent, adding complexity. Reliability enhancement features for storability range from simple expiration date stamps, to positive/negative controls and calibrations built into the assay themselves, to passive color-change devices that indicate to the user that the cartridge has exceeded allowed safe storage temperatures prior to its' insertion into the analyzer.

Another major design challenge is the selection of an assay readout method. Existing coagulation assays detect fibrin polymerization via sample turbidity, optical scattering, conductivity or viscosity, while thrombin and fibrin production can be directly monitored by colorimetric and immunological methods (based on antibodies bound to a membrane or dispersed nano-particles). Many of these methods are slow, require physical separations, or are not well suited to implementation at the microfluidic scale (10-100 μm). Of particular interest, in colorimetric assays, a colorless substrate is cleaved into a light absorbing form by either: (1) the enzyme complex that produces thrombin, or (2) by thrombin itself. In these two types of assays, the amount of absorbed light versus time may be assumed to be proportional to, in the first case, thrombin (as it is produced at a proportional rate), or in the second case to fibrin (the result of thrombin's enzymatic activity). While such assays are fast and relatively straightforward, they have two features that are undesirable in a microfluidic device: first, plasma must be separated to remove the absorption signal from the red blood cells, and second, the degree of absorption decreases linearly with the sample thickness, and could be undetectable for a 10 μm thick sample.

Your design team may assume, as a baseline, a modified colorimetric assay, where the cleavable chromogenic reagent is replaced with a fluorogenic one; that is, once cleaved by the enzyme, a non-fluorescent pre-cursor becomes fluorescent (i.e., it absorbs light in one range of wavelengths and re-emits the energy as light of a longer wavelength.) Thus, as with the colorimetric assay, thrombin of fibrin concentration may be followed in time by measuring fluorescent intensity. The resulting assay should have superior sensitivity in thin samples, and it may be possible to achieve acceptable results without red blood cell separation. If possible, excitation will be provided by diode-based light sources, and fluorescence will be detected by either a CCD detector or an array of discrete photodiodes.

To derive useful PT, APTT and APCR data, several such fluorogenic measurements will need to be performed at different dilutions of blood, sera, and co-factors. Including controls and in situ calibrations, each cartridge will need to perform 20-50 separate batch reactions. In the interest of time, these reactions will likely need to be performed in parallel. This does not provide a major obstacle, however, as the cost of microfluidics (like microelectronics) scales with the die (chip) size more than the complexity of the circuitry within. Rather than 20 or more identical units in parallel, it may be advantageous to use a simple mixer/diluter to obtain a dilution series of a single co-factor, to reduce the number of units to one for each of the PT, APTT and APCR assays.

Reference

"Microfluidic Large-Scale Integration," *Science*, Volume 298, Issue 5593, 18 October 2002, pp. 580-584

Vendors

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Agilent (lab on a chip): http://www.chem.agilent.com/Scripts/PCol.asp?lPage=50
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A-IIS.6.3 Screening of Kinase Inhibitors [PROD]
(John C. Crocker, University of Pennsylvania, January 2007)

Background: A promising class of cancer therapeutics are kinase inhibitors (KIs), small molecule compounds that reduce the phosphorylation activity of one or more of the ~500 kinase enzymes in the human body (examples include gleevec, temserolimus, gefitinib, staurosporine, ...). To be useful, a KI must be specific—targeting one or a small number of kinases, without significantly affecting the activity of the others. It has been estimated that pharmaceutical companies are currently spending ~$100M/year screening potential therapeutic KI compounds created by their drug discovery efforts.

In general, each kinase is a protein which phosphorylates a specific protein or set of proteins, affecting their function much like an on/off switch. Along with phosphatases that remove phosphate groups, these enzymes are largely responsible for the biochemical regulation within living cells. In general, the reaction resembles:

$$\text{kinase} + \text{protein} + \text{ATP} \rightarrow \text{kinase} + (\text{protein})\text{PO}_4 + \text{ADP}$$

That is, the kinase binds adenosine tri-phosphate and an active site on a target protein, moves one phosphate group onto the target and unbinds. As an enzyme, the kinase is not modified and repeats the reaction as long as target protein and ATP are available. About 100 kinases have been cloned to date and may be considered commercially available for the purposes of this project. In the lab, a short peptide is usually substituted for the target protein, (potentially a different one for each kinase), as peptide synthesis is simpler than protein expression and purification.

The KI competes with the protein/peptide by binding to the kinase (usually its ATP binding site). The strength of inhibition is characterized by its 'inhibition concentration 50%', IC_{50}; that is, the KI concentration at which a given kinase's activity drops by 50%. The IC_{50} is typically determined by performing a few assays (~5-10) varying the KI concentration over several orders of magnitude, and finding the cross-over (if any) in the resulting "S"-shaped curve of kinase activity. The potency of the KI increases with lower IC_{50} values. Specificity of a KI is characterized by its having a low IC_{50} concentration for one kinase, but much higher IC_{50} values for all other kinases; a therapeutic dose could then be set just above the low IC_{50} for the kinase to be inhibited, but not so high as to affect the other kinases in the body.

Currently, most of these assays are performed in-house by large-scale, automated, robotic fluid handlers operating on arrays of well-plates. The incremental cost of such assays (i.e., reagents only, neglecting the cost of the fluid handler, personnel, and lab space) has been reported to be about $0.20 per IC_{50}. To save costs, KI compounds are often first screened against ~20 kinases which are representative of the major kinase families, and only those few passing muster are screened against the full battery of 100 kinases. Even with this price level and staged approach, assay costs are a significant current bottleneck to drug discovery.

Business Model: This project is to design a 'small start-up' scale company/facility to perform standardized kinase inhibition assays on compounds sent from the drug-discovery groups at large pharmaceutical companies. The large number of drug candidates these groups create, along with the large number of different kinases in the human body leads combinatorially to a very large number of inhibition screens that need to be performed. To attract your big pharma customers to contract their inhibition assay work to your company, you will need to undercut their current incremental assay cost significantly: assume a price of \$0.05 per one compound/one kinase IC_{50} assay. Target plant capacity should be about 1MM IC_{50} assays per day. This corresponds to about 250MM assays/yr (assume personnel have an 8 hr day, 5 day/wk schedule), \$12.5MM annual gross revenue, and less than a third of the current market demand. To compete effectively with an in-house system, you should complete all assays within 3 business days or less (delivering the results electronically) and provide staged-assays: the customers can specify assays against a fixed subset of 20 kinases, the full 100 kinase set, or a conditional approach. For simplicity, it may be assumed that the customer delivers their KI compounds bulk-loaded into microwell plates in a standard format. Moreover, assume that all reagents can be purchased commercially or easily synthesized in house using bench-scale equipment. Financial analysis should be based on a staged funding basis, with a biotech startup-appropriate investor's rate of return (IRR) for each stage.

Design Proposal: The required throughput (5-10MM separate batch reactions per day, or about 100 per second) and small revenue per assay precludes both conventional robotic fluid handling and low-speed 'lab-on-a-chip' methods. Instead, each batch reactor will be a single aqueous droplet, a few tens of microns in diameter, floating in a carrier oil, in which the droplets will not spontaneously coalesce. At this scale, the 10MM droplets/reactors needed for a day's production will have a total volume of significantly less than 1 ml. The difficult part is to fabricate the 10MM droplets containing the different KIs, kinases and reactants at the required concentrations, and to read out the kinase activity, and perform both of these steps fast enough to keep up with the schedule.

Similar to other high throughput techniques in molecular biology, such as phage display, we will not maintain strict control over the location or contents of every reactor droplet. Instead, we will rely on a statistical approach. For example, if we want to assay 100 KIs against 100 kinases (i.e., 10,000 combinations), we will fill one test tube with 50,000 drops, about 1% of them each containing a given KI, and a second test tube with 50,000 drops, about 1% of them each containing a given kinase. If we now randomly select pairs of droplets, one from each tube or 'library', and fuse them together, each droplet will realize a single kinase/KI reaction. Statistically, we expect to perform all 10,000 reaction combinations with equal probability. By using 50,000 rather than 10,000 fused droplets, we produce about 5±2 replicates (a binomial distribution) of each reaction, ensuring that very few reactions are 'missed'.

The first challenge that arises is how to read out kinase activity from so many microscopic droplets. After the fused droplets have been incubated at 37°C for a standard reaction time, the amount of ATP depletion or ADP production provides a measure of kinase activity. Several non-destructive, non-contact methods for reading out ATP/ADP reactant concentration have been developed, such as fluorescence depolarization photometry (FDP) and fluorescent resonant energy transfer (FRET). For example, in the 'Transcreener' FDP process, a fluorescent ADP homolog 'probe' is first bound to a custom designed antibody. ADP from the kinase reaction displaces the 'probe' from the antibody binding site, and the ratio of free to bound probe can be determined using fluorescence polarization. Commercial flow cytometers can serially read out fluorescence polarization of 10 μm droplets at speeds up to ten thousand drops per second; reading out the kinase activity in our 50,000 droplets example would only require 5 seconds!

The second, bigger challenge, is after kinase activity has been read out, how do determine which KI and kinase were loaded into the droplet initially. In this field, what is needed is called a ‘barcode’, conceptually similar to the unique UPC codes used in the grocery store. That is, prior to creation of the two emulsion libraries, each KI and kinase will be mixed with a ‘barcode’ whose unique character can also be read out by fluorescence in a flow cytometer. While several barcode technologies are in development (e.g., DNA barcodes and nanowire barcodes), for this project the barcodes will consist of combinatorial mixtures of colloidal particles with varying fluorescent emission wavelength and intensity. Each fused droplet will contain these colloidal particles corresponding to two ‘barcodes’, one for the KI and one for the kinase. Presumably, reading the barcodes can be done at a comparable speed to the kinase activity measurement above, but details and optimization are to be worked out by the design team.

Overall, the process can be divided into: (1) unpacking of well-plates from the customer, and loading the compounds into the emulsification equipment, (2) fabrication of ‘barcoded’ KI and kinase emulsion libraries, (3) mixing/fusing the libraries together, (4) incubation at 37°C, and (5) reading out both the kinase activity and ‘barcodes’ of all the fused droplets. (Unlike the example above, the KI library will also need to contain several different dilutions of each KI, to allow construction of an IC_{50} curve). Step 1 will need to be performed by a robotic fluid handler. Steps 2 and 3 will be performed using high-speed, electronically gated emulsion ‘gun’ devices from Raindance Technologies, with throughputs and costing estimates available from that company. Much of the team’s design work and optimization will be constrained by step 5, the complicated task of reading the barcodes in each micro-droplet to identify both its kinase activity and which inhibitor and kinase it contains. Two different readout architectures are to be considered. The first is a long capillary through which the droplets move single file, between different temperature baths and flow cytometers. The second loads the droplets into a small transparent platter, which is then rotated and read out like a CD or DVD. In both cases, throughput will be limited by either fluid transport or fluorescent readout noise.

In addition to financial analysis, the design team will need to concern itself with modeling the reaction thermodynamics and kinetics of inhibition assays, optical detection and fluorescence signal-to-noise, combinatorial issues with the barcodes, and scheduling issues both on the assayer and plant level, as well as the fluid transport of droplets through channels at high speed.

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Raindance Technologies: http://www.raindancetechnologies.com/

Caliper Life Sciences: http://www.caliperls.com/

Alpha Innotech (scanners):
http://www.alphainnotech.com/productfiles/prodoverview.asp

A-IIS.6.4 High-Throughput Lung Cancer Genotyping [PROD]

(John C. Crocker, University of Pennsylvania, January 2008)

One in seven deaths in the U.S. is due to lung cancer. An emerging strategy to treat cancer is based on the development of pharmaceuticals, such as kinase inhibitors, that specifically block the altered signaling pathways that promote cancer cell proliferation. Because the mutations causing even one type of cancer vary among different patients a given pharmaceutical may be highly effective in one patient and completely ineffective in another. While current treatment strategies are altered depending on the presentation of the patient and analyses of biopsied tissue, much room for improvement remains. The ultimate limit of such a tailored approach to therapy is *personal medicine*; where, for example, cancer cells are subjected to detailed gene sequencing, or *genotyping*, to identify the specific biochemical changes present in the patient's tumor. This genetic information can then be applied to design an effective treatment based upon either prior clinical experience, or perhaps in the more distant future, using a rational approach based upon biochemistry. Such personalized treatment for lung cancer is beyond the current state of the art: only a few dozen mutations have been identified and only a few such drugs are ready for the clinic.

This problem is to design a high-throughput process to genotype lung cancer cells from clinical patients, to develop a corresponding clinical/business model in the context of a small biotech startup company, and assess its financial viability. Specifically, the team is to assay 500 predetermined point mutations among several different relevant genes for each patient sample, and to electronically deliver the report to the clinician within two business days of sample receipt. A significant market is expected: there are more than 160,000 new diagnoses of lung cancer in the U.S. per year, and a genotyping price of the few thousand dollars per patient is likely reasonable. The financial analysis should assume a roll-out market scale of 20,000 patients per year and a step increase to 100,000 per year three years later (e.g. 60% market share after genotyping becomes a standard of care).

At first glance, it seems that quantitative polymerase chain reaction, or qPCR (e.g the TaqMan^{TM} assay by Applied Biosystems [1]) is well suited to the problem of precisely quantifying small numbers of mutations from a large number of samples, especially if the samples contain a mixture of both cancerous and healthy cells. High-throughput implementations of qPCR are typically based on a well-plate, robotic fluid handler technology platform. This approach has limited throughput due the large number of fluid handling steps required, as well as relatively high capital costs and reagent costs per assay. Recently, Fluidigm [2] has introduced a microfluidic system for qPCR, termed BioMark^{TM}, with much improved throughput and 10 nanoliter reaction volumes. The base-case design for high throughput genotyping will use this commercially available platform.

Conventional PCR is a temperature controlled, cyclical reaction in which a targeted DNA sequence in a sample is 'amplified', or nominally made to double in concentration during each thermal cycle. Each reactor contains a DNA sample, short oligonucleotides (primers), DNA polymerase (e.g., Taq polymerase) and triphosphate nucleotides required by the polymerase (dNTP) to synthesize new DNA. The sequences of the two primers are chosen such that they are complementary to the sample DNA at two locations a few hundred bases apart straddling the target sequence, on opposing strands. During the high temperature portion of the cycle, the double stranded DNA thermally dissociates into two separate single strands. Upon cooling, the primers hybridize to the complementary segments of the sample DNAs. The short double stranded segments created by the primers bind the polymerase, which rapidly synthesizes a complementary daughter strand by extending the double stranded target segment one nucleotide at a time. After this extension is effectively complete, the sample is reheated, melting the double stranded segment, yielding twice as many copies of the original target DNA as in the previous cycle. An essential and useful property of PCR is that only the DNA sequence between the two primers is amplified—PCR is selective enough and sensitive enough that it can amplify even a single molecular copy of the target sequence mixed in with billions of bases of other DNA, allowing the detection of known 'needle in a haystack' DNA sequences in samples containing genomic DNA or massive bacterial contamination.

The purpose of quantitative PCR, or qPCR is not mere detection/replication of a DNA sequence in a sample, but the quantification of how many copies were present in the original sample (present at such low concentrations amid other DNA that direct detection is presumably impossible). In principle, if the amplification led to an exact doubling per thermal cycle, one could readily work backwards from the final concentration and number of cycles to compute the initial concentration. In practice, depending on how well the primers, reaction temperature and incubation times have been optimized, the effective amplification per cycle may be less than two. Moreover, once the sample has been amplified significantly, amplification will become linear or cease altogether due to depletion of the dNTP reactants. For this reason, in qPCR one quantifies the amount of amplified DNA in the sample after each thermal cycle to determine the concentration while amplification is still in the exponential phase. A high-throughput qPCR system obviously requires a non-invasive, optical probe of how much of the target sequence has been produced. While the optical signal will presumably be zero (i.e. background noise) for the first several cycles, it will rise above the background level while the amplification is still exponential (prior to NTP exhaustion and the slowing of the reaction). This data can then be analyzed using an exponential growth model, and the starting concentration determined by extrapolation.

Several optical techniques exist for reading out the target concentration in qPCR. For this project, the team will use the TaqMan^{TM} assay, shown schematically in Figure A-IIS.14, originally developed by Roche. In this approach a third DNA strand is prepared which is complementary to the target strand in the middle of the sequence. This DNA probe is modified to contain two extra molecules: one a fluorescent tag and the other a quencher that de-excites the fluorophore by fluorescent energy transfer (FRET) when the two molecules are close together. As originally prepared, the DNA probe is non-fluorescent due to the juxtaposition of the dye and quencher. During PCR thermocycling, however, the probe strand hybridizes the target sequence and 'gets in the way' of the Taq polymerase trying to extend the daughter strand. A useful feature of Taq is that it cleaves a few bases off any strand that gets in it way; that is, it has a native exonuclease activity. By placing the dye and quencher appropriately on the probe DNA, we can arrange Taq to cleave them apart, with the net effect of creating one fluorescent (unquenched) dye molecule for every DNA target strand that Taq has produced. This fluorescent signal can then be read out directly, one per thermal cycle.

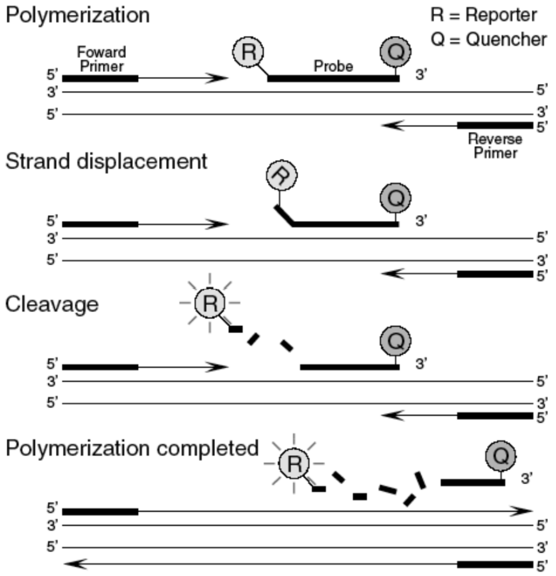

Figure A-IIS.14. Schematic of TaqMan assay within a PCR cycle. A probe strand containing a fluorescent reporter and quencher modification. As the polymerase Taq extends the forward primer, it encounters the probe strand, cleaving it to fragments (exonuclease activity) and displacing it from the template strand. The cleaved fluorophore is then fluorescent.

In the Fluidigm BioMark^{TM} system [2], a pneumatically activated microfluidic chip containing a 48 by 48 square grid of 10 nl reactors is integrated into a standard well plate. The chip is loaded by dispensing reagents into 96 wells on the carrier using a robotic fluid handler. For this design, DNA samples from 48 patients might form the rows, and 48 different primer sets might form the columns, and one chip could produce qPCR data for 48 patients at 48 gene loci. After the reagents have been dispensed, the chip is loaded into a NanoFlex^{TM} instrument, where the chip is activated pneumatically to mix the reagents and load the nanoreactors. Once this is complete, the chip is removed and moved to the BioMark^{TM} thermocycler instrument with an integrated fluorescent plate reader. The CCD based imager to measures the qPCR signal in all 2,000 nanoreactors in parallel, once per thermal cycle.

Given that the core technology is commercially available, much of the design project will be concerned with modeling the qPCR reactions themselves, including designing specific primers and reaction conditions for at least five known lung cancer mutations, such as those associated with the tyrosine kinase (TK) domain of epidermal growth factor receptor, EGFR. Since two inhibitors to EGFR-TK have been clinically approved, gefitinib and erlotinib, a considerable literature on the corresponding mutations and their frequency is available. The second major part of the design study will concern the consideration of alternative high-throughput genotyping technology, such as DNA microarrays (e.g. the GeneChip^{TM} assay by Affymetrix [3]) and DNA bead arrays (e.g the BeadArray^{TM} by Illumina [4]). Given the fact that potential competitors using these other assay methods already exist [5,6], estimates of their costs and research regarding their assay quality/sensitivity will also be performed. If the cost competitiveness of BioMark-based qPCR appears marginal, then assay quality and sensitivity will become major design drivers for this project, otherwise the financial analysis will focus on optimizing return on investment.

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A-IIS.6.5 Rapamycin-Coated Stents for Johnson & Johnson [PROD]
(Scott L. Diamond, University of Pennsylvania, January 2002)

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 ε-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.

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A-IIS.6.6 High-Throughput Screening of Clopidogrel Resistance using Microfluidic Tech. [PROD]

(Scott L. Diamond, Univ. of Pennsylvania, 2009)

Develop a point-of-care (POC) device that uses disposable microfluidic cells to test for patient resistance to the anti-platelet agent, Plavix. Plavix can reduce adverse clotting events during angiography, but some patients are poor responders to the drug and require higher doses to gain protection.

Platelet aggregation assay is now conducted in a tube with a stir bar to evaluate Plavix function. Design a microfluidic cell that exposes whole blood under controlled laminar flow to a thrombotic surface stimulus. Develop an automated machine that runs the microfluidic cell to allow quantitative testing of a sample of drop of blood (< 1 mL). The end user should only deliver blood to the microfluidic cell and place the cell in the POC device. The microfluidic cell is then disposed of as biomedical waste.

1. Evaluate: Market size in terms of placed (POC device) and microfluidic cells/year for U.S. and European markets.

2. Design the microfluidic cell to perfuse whole blood over a patterned surface at controlled wall shear rates of 100 s^{-1}. Often fluorescence imaging is a fast low cost analytical technique.

3. Design a POC unit that deploys the microfluidic cell and returns an evaluation in < 10 minutes. Assume an OEM will place your logo on the machine.

4. Develop a manufacturing process to manufacture the microfluidic cells.

5. Determine profitability of such a device and sales of microfluidic cells.

<u>NOTE</u>: This project may require laboratory work for characterizing the microfluidic devices.

A-IIS.6.7 $100 Genome using Raindance Technology [PROD]

(John C. Crocker, Univ. of Pennsylvania, 2011)

The first human genome was published in 2003, and was the result of over $3 billion of public funding for the Human Genome Project (HGP). Around the same time, a privately funded company, Celera Genomics, using superior technology, published its own genome for just one-tenth the cost: $300 million. The content of a single human genome has immense utility as a research tool for understanding the molecular origin of disease. Currently, many researchers are focused on even a greater opportunity and technical challenge—personalized medicine. If the specific genome of an *individual* is known, then it can be used to predict their future predilection for different diseases, or to tailor more effective life-saving therapies for them, e.g., for cancer.

One impediment to personalized medicine is the current high cost of genotyping: you can have your complete genome sequenced today commercially [1], but it comes with a price-tag of $350,000. To stimulate further progress, in 2006 the X Prize Foundation announced the *Archon X Prize for Genomics* [2], which will award $10 million to the first team to sequence 100 different human genomes, for less than $10,000 apiece, in less than 10 days, with an error rate below ten per million bases. Several firms have started working toward the challenge, including *454* Life Sciences, Pacific Biosciences and Helicos Biosciences [3]. These companies make frequent reference to the '$1000 genome' and are expected to make the first X Prize claims any day now.

While these whole genome technologies are exciting, a larger impediment looms to threaten the idea of personalized medicine—*a complete lack of clinical data*. In total, only a few dozen genetic polymorphisms that interact with clinical treatments have been discovered to date, and sequencing just those polymorphisms costs a negligible amount. The most basic assumption of personal medicine is that if we had a large enough data set of whole patient genomes, we could discover millions of interactions between polymorphisms and clinical outcomes for different treatments via simple correlational data-mining. The central question is who will construct that dataset? The most plausible candidate is the large pharmaceutical companies themselves. Today, dosage decisions and safety contra-indications for pharmaceuticals are based on large data sets formed during clinical trials, at a cost of ~$10,000 per participant. If the cost of producing a whole genome was reduced to a few hundred dollars, then complete patient genotyping could become a standard practice during all clinical trials; essentially piggybacking the construction of a personal medicine database on the existing infrastructure.

This project is to design a '$100 genome' process within the context of a small startup company using the microfluidic emulsion microreactor technology commercialized by Raindance Technologies [4]. Raindance founder David Weitz has disclosed internal estimates that suggest per genome costs as low as $30, or *seven orders of magnitude cheaper* than the Celera technology of a decade ago. The team's business model will be a service company, receiving large numbers of patient samples (e.g., cheek swabs) from a pharma company client, and the electronic delivery of the corresponding whole genome data to the client within 30 days of sample receipt. Product sequences should have an error rate of less than ten parts per million for non-repeating intronic sequences. The core (Raindance) technology consists of integrated fluidic systems that create, handle, combine and optically scan microscopic aqueous droplets flowing through oil-filled fluidic channels. Each droplet is in essence a tiny microreactor that can be used to perform the same biochemical assays conventionally performed at the lab bench with test tubes and pipettes, or on the well plate scale with automated fluid-handling robots. The tiny scale of the droplets dramatically decreases material costs, and allows higher throughput processing than possible for macroscopic robotics, single micro-devices can process 10^4 droplets per second.

The sequencing approach announced by Weitz's new startup GnuBio [5], and to be used as a baseline starting case by the team, is based upon the Watson-Crick base-pairing (hybridization) of a library of all 6 base oligonucleotides to roughly 1 kilobase (kb) fragments of patient DNA. By detecting which of the 4,096 oligos bind the patient fragment, it is possible to reliably reconstruct the fragment sequence using standard bioinformatic algorithms. To use this assay in a microfluidic platform, one will first have to create a library of droplets each containing just one of the 4,096 oligos along with a distinctive fluorescence 'barcode' identifier. Second, individual molecular fragments of patient DNA will be PCR amplified in large droplets (>1 nanoliter) that will then be broken down into thousands of smaller (~1 picoliter) droplets, each containing many copies of the original fragment. Third, these droplets will then be merged in a 1:1 fashion ('crossed') with the oligo library droplets. The merged droplets will be arrayed on a flat slide, and incubated to allow hybridization to occur in those droplets where the oligo finds a 6-base complementary section in the patient fragment. Hybridization will be detected by standard optical means such as Fluorescence Polarization (FP) or Fluorescent Resonant Energy Transfer (FRET). High throughput scanning of hybridization and droplet barcodes (to identify the oligo) will be required—Weitz estimates that existing CCD cameras and mechanical scanners should be able to effectively scan 10^6 droplets per second. Since the human genome contains roughly 3 billion bases, many millions of 1 kb patient fragments will need to be sequenced in this way, and then stitched together using other bioinformatic algorithms into a full sequence.

Like all whole genome sequence schemes, the Weitz/Raindance approach must minimize capital (for scanners), maximize throughput (minimize droplets scanned per sequenced base) and have an effective barcoding scheme (that simplifies scanning). In addition to analyzing the GnuBio strategy, the design team will also devise and investigate other sequencing/scanning approaches. For example, to minimize the number of droplets that must be formed and arrayed, one approach is to sequence entire fragments in each droplet via the optical readout of synchronous base additions, such as in the Helicos sequencing technology. In this approach [6], bases are added to a daughter strand one base at a time by a polymerase, with external synchronization of polymerases using an acid or UV cleavable modified nucleotide. This should allow many bases of sequence to be read out per droplet, as well as eliminate the need for any barcoding whatsoever, greatly simplifying and speeding scanning. To reduce capital costs associated with cameras and mechanical scanners (identified as challenges by earlier Penn design teams), one idea is to use a microfluidic substrate resembling a DVD that can be sealed after loading, rotated at high speed and read out by a simple 'point scanning' optical head. While such a design process is potentially rather open-ended, it is expected that the team will quickly settle on a single most attractive sequencing approach. The team's approach and the Weitz/Raindance approach will then both be subjected to more intensive analysis and comparison of costs/throughput. An emphasis will be placed on process design to optimize sequence throughput as well as relevant biochemical reactions/kinetics, microfluidic fluid mechanics/network layout and fluorescence signal to noise, as all limit and determine ultimate throughput and cost. All sequencing approaches will need to be validated by bioinformatic reconstruction of mock data, most likely using the bioinformatics toolkit in MATLAB. Some of the raw data will contain errors due to finite signal to noise in fluorescence measurements, and the team will need to verify that these errors can be weeded out robustly to allow a final error rate of less than 10 parts per million in the final product sequence.

Since winning an X prize is not an acceptable business model, the team will evaluate the viability of a small venture capital funded biotech start-up, serving large pharma companies as their clients. The team will assume a Series A funded period in which the technology is demonstrated at a scale comparable to the X prize rate—10 genomes/day * 250 days/year = 2,500 genomes/yr. The team will determine their market price per genome based upon their own incremental and capital costs, as well as those estimated for their two closest competitors, but this is expected to be in the $100-300 range. After Series B funding, the assumed throughput with be quadrupled to 10,000 genomes per year. The financial analysis should seek a significant, positive NPV over a total four-year time horizon with an appropriate IRR for a biotech startup with VC funding. Acceleration of genotyping volume can be considered if market analysis suggests adequate demand. If the overall financial analysis looks favorable, the team should also estimate the capital requirements to expand their operational throughput to a plausible ultimate demand (after the widespread adoption of personalized medicine) of 10^6 genomes/year.

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A-IIS.6.8 Blood Processing Unit [PROD]
(Scott L. Diamond, Univ. of Pennsylvania, 2012)

Background

Preclinical and Clinical trials often involve the collection of numerous samples of blood that must be prepared for flow cytometry to obtain platelet, neutrophil, and red blood cell counts as well as prepared for storage of stable serum and plasma samples. Furthermore, neutrophils can be prepared in a stabilized lysate for later preparation of DNA in a clinical lab. Assume the unit can sell for \$100K and the cartridge is \$25. Also, assume 50 % penetration after 3 years of a total clinical trials blood processing market space of 1000 clinical sites in the country that process 1 million blood samples a year.

Design specification

Design a system (cartridge and processing unit) to automatically process a sample of citrated human whole blood (5 mL) and provide the cell counts and three output tubes (> 100 uL plasma, > 100 uL serum, and neutrophil lysate with >100,000 neutrophils) within 15 minutes. Design a disposable cartridge to accept a 5 mL vacutainer of citrated human whole blood. The cartridge will contain all the reagents, wells, tubing, disposable pipettes, and microfluidics for processing the sample. The processing unit will contain all hardware (optics, magnets, pumps, etc.) to run the cartridge. At the end of the process, the 3 output tubes are removed from the cartridge and the cartridge is disposed of as biomedical waste. The processing unit should be no larger than a desktop computer tower and simply plugs into an electrical outlet (no waste fluid containers). The cartridge should be as small as possible to achieve the design specification, but no larger than 4” x 6” x 3”. Also consider inventory issues that the cartridge should be stable at room temperature for at least 6 months.

Background

Human blood will normally clot when taking out of the body, however citrate is a calcium chelator and prevents the formation of tenase (XaVa) which generates thrombin and causes blood to clot. Typically, cell counting is achieved by passing single cells through a laser and measuring fluorescence. Fluorescent antibodies to label platelets, neutrophils, and red blood cells (RBCs) are widely available. Cells are typically separated by centrifugation at various speeds, however novel approaches could include immunomagnetic separation or plasma skimming microfluidics. Various reagents are available for licensing (from Qiagen for example) but must be accommodated on the cartridge. Think of your cartridge as a self-contained batch processing chemical plant that has all feed and product streams residing on the cartridge.

Possible Competitors and/or Co-Developers: BD, Becton-Coulter, Qiagen, Roche, Dade-Behring.

Reference

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A-IIS.6.9 Clinical Testing of Citrated Blood [PROD]

(Scott L. Diamond, Univ. of Pennsylvania, 2013)

Most clinical blood samples are collected in citrate which chelates calcium, magnesium, and zinc ions. This prevents clotting of the sample. In order to study clotting (thrombin production), a high concentration calcium chloride buffer (10-20 mM) is added to the blood (“recalcification”) which allows for the formation of thrombin and consequent clotting. Interestingly, magnesium and zinc are not typically restored and their absence has unknown effects.

Develop a microfluidic device to add and mix a Ca/Mg/Zn buffer into citrated whole blood and then split that blood into multiple flow streams for testing of blood clotting on three distinct surfaces (collagen, collagen+kaolin, collagen+tissue factor). A novel fluorogenic thrombin sensor is available for measuring in situ thrombin production. In this project, expect to design and fabricate a microfluidic device to conduct mixing and clotting studies.

Develop a business model for monitoring patients receiving direct thrombin inhibitors (DTI; dabigatran), direct factor Xa inhibitors (apixaban), or a $P2Y_{12}$ inhibitor (Plavix, an anti-platelet agent). Assume participation in a 50,000 patient clinical trial as part of the product rollout. Also assume a growing market for rapid testing of blood from trauma patients at risk of bleeding.

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A-IIS.6.10 Stem Cell Therapy for Spinal Cord Injuries [PROC]
(Tiffany D. Rau, Eli Lilly, Puerto Rico, 2014)

Overview
Design a manufacturing facility for the production of a stem cell treatment for spinal cord injuries. The manufacturing facility will also produce the material in custom-designed vessels that the team will design for the culturing of the stem cells.

Description

You are part of a small to midsize biotechnology company that focuses on cell therapies for a number of indications. Your company has one launched product, but it is not in the cell therapy area.

Your company is currently developing a spinal-cord injury, regeneration therapy that will allow patients to recover from their injuries and be able to move again. There is currently an unmet need in the market for the treatment of spinal cord injuries yielding significant functional improvements. Spinal cord injuries are diverse and are typically permanent leaving a patient with a lower quality of life. There are approximately 250,000 people in the US with spinal cord injuries, with an additional 12,000 people/year are added in the US alone (California's Institute for Regenerative Medicine).

A research team has been pursuing two different cell therapy systems. One uses human embryonic stem cells (hESC) and the other uses adult stem cells. Both are at the same stage of development. As part of the commercialization team, you will need to decide whether to progress the hESC or adult stem cell therapy to market – resources are limited and time is of the essence.

Once your team decides on the platform, you will design a new manufacturing facility/suite needs to be constructed. hESC and adult stem cells are very delicate cells and are typically attached cell lines so it is difficult to grow them in traditional bioreactors/fermenters which are normally designed for suspension cultures. Also note that the therapy is the "cell" itself – so you need to ensure that the cells are not damaged in the production process. It is suggested that you design a new-type of low-shear bioreactor system that controls pH, dissolved oxygen, and temperature. There are systems on the market for growing attached cell lines as well as stem cells, but your company wants a custom scale-up solution for its cell-therapy division. Your company would like you to review what is on the market and then create/optimize a bioreactor system to produce the spinal-cord injury treatment under GMP conditions.

Your manufacturing process will include everything from vial thaw to purification, but final formulation and packaging will take place offsite and should only be mentioned in your report. On completion of this project, you will have designed the process, the new bioreactor to grow the cells in, and the production facility to make the life-improving cell therapy for spinal cord injuries. A diverse team of engineers, scientists, regulatory experts, as well as business leaders has been established to help you deliver on your project. Your project is on the critical path and your patients are waiting.

Important information. Please Read Before Selecting Problem

The creator of this project is not based in Philadelphia so many if not all interactions with the students will be by SKYPE, phone and email. Also the meetings will be at mutual agreeable times, but may not necessarily be between the times of 9 am and 5 pm EST. When selecting this problem, please take this into consideration as interactions will be remote. Please note that in today's world it is not unusual for interactions to be remote. The creator has delivered projects around the world while not being at the location.

Helpful/Interesting Information

Examples of cell therapy companies: Biotime, Cellular Dynamics, Celgene, Geron, Mesoblast, Lonza, and many more.

You may find that the Biopharmaceutical SUPERPRO Designer example on Intelligen's website www.intelligen.com helpful as you create your design project. Please note that the model works using their evaluation version which is downloadable on their website. The evaluation version of the software does not allow the user to print or save files.

The FDA has given suggested guidelines for the internal layout of a biopharmaceutical facility/vaccine facility – so you may wish to refer to their website for guidance. www.fda.gov

Industrial trade publications: BioPharm International, BioProcess International, Pharmaceutical Manufacturing, Genetic and Engineering News (GEN), and many more.

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A-IIS.7 POLYMERS

A-IIS.7.1 Polyvinyl Acetate Production for Polyvinyl Alcohol Plant [PROC]

(Frank Petrocelli and Steve Webb, Air Products and Chemicals, 2000)

A grass roots facility to produce polyvinyl alcohol (PVOH) is being constructed in a chemical complex on the U.S. Gulf Coast. Your design team will complete the process engineering for the unit which produces polyvinyl acetate (PVAC). PVAC is further reacted in another part of the facility to produce the PVOH final product. The polyvinyl acetate unit includes the polymerization reactor system and the downstream recovery process. Your design must be capable of an annual production rate of 100 MMlb of PVAC intermediate.

PVAC is produced by the free-radical polymerization of vinyl acetate. Your company, PolyPenn, Inc., has experience and process knowledge using a continuous solution polymerization in which the solvent is methanol. The process uses a thermal initiator, which costs \$5.00/lb. The decomposition kinetics for the initiator are given by the following expression:

$$d[I]/dt = - k_d * [I]$$
$$k_d = 1.4E12 * \exp(-23{,}900/RT)\ s^{-1}$$
$$R = 1.9872\ \text{cal/(mol-K)},\ T \text{ is in K}$$

To a first approximation, the polymerization follows classical free-radical polymerization kinetics (as described by Flory; see references by Billmeyer and by Finch). Reaction conditions must be chosen to produce a medium-molecular-weight grade of PVAC, defined as a grade having a number-average molecular weight of 130,000 (i.e., the number-average degree of polymerization, X_n = 1,500 repeat units per polymer chain). Again, the references by Billmeyer and by Finch contain mathematical expressions for determining the polymer molecular weight as a function of reaction conditions. The reaction temperature must be maintained between 145 and 180°F, and the reaction pressure must be < 15 psig (this combination of conditions has been shown to reduce the possibility of a runaway reaction in the event of a process upset). Also, for safety concerns (to limit the amount of reacting material), the maximum size of any single reactor will be 10,000 gal.

Several decisions must be made in the initial design to choose among options for the process. Typically, the reaction does not proceed to complete conversion. The molecular weight of the final PVAC is influenced by the level of conversion (higher conversion lowers molecular weight) and the concentration of methanol in the reactor (increasing methanol lowers molecular weight). The polymerization can occur in a series of polymerization reactors. Your design team must decide on the type of reactor (i.e., CSTR, PFTR, recycle loop), the number of reactors, reactor size, and the method of heat removal (cooling jacket, cooling coil, and/or overhead condenser). Increasing the reactor size and the number of reactors can allow higher conversions for a given molecular weight, which would reduce recovery cost for the monomer. Obviously, there is a trade-off between the recovery cost and increased capital cost. Additionally, increased reactor size may reduce initiator use and cost. Your objective should be to find a design which achieves a minimum total cost over the entire plant life.

After the polymerization reactors, the unreacted monomer must be removed from the polymer stream. In your company's existing polymerization units, the monomer is removed in a distillation/stripping column. Methanol vapor is fed to the bottom of the column and a mixture of methanol and vinyl acetate monomer is taken as an overhead product. The PVAC exits from the bottom of the column in a methanol solution. To minimize product color formation, column temperatures should not exceed 240°F. The bottoms from the PVAC/methanol column must have a solids content of 36 to 40% to be suitable for existing processing equipment downstream.

Some of the overhead product can be recycled and mixed with the reactor feed; the fraction which can be recycled is dependent on its composition. Excess overhead product is separated into pure vinyl acetate and methanol in a separate, existing recovery process - assume a processing cost of \$0.005/lb of recycle for this operation.

Ample cooling water is available at a supply temperature of 90°F and must be returned no higher than 110°F. Cooling water cost is \$0.50/1,000 gal. Saturated steam is available at 150 and 600 psig. The cost of steam is \$5.00/MMBtu. Electricity is available at a cost of \$0.05/kWh. Use the market price for the cost of raw materials.

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A-IIS.7.2 Butadiene to Styrene [PROC]
(Bruce Vrana, DuPont, January 1997)

Butadiene (BD) is produced by the expensive extraction of BD from a crude C4 stream in an ethylene plant. The BD value is about \$0.06/lb when it is contained in the crude C4 stream, but about \$0.18/lb after it is extracted. Because of this price difference, processes are always being sought to use the BD in the crude C4 stream without extracting it, and returning the remaining C4 stream to the ethylene plant. A typical crude C4 stream has the following composition in weight percent:

30%	BD
30%	isobutene
20%	1-butene
7%	*cis*-2-butene
7%	*trans*-2-butene
4%	*n*-butane
2%	isobutane

Dow has developed a process to dimerize the BD in a crude C4 stream to vinylcyclohexene (VCH) using a proprietary copper-loaded zeolite catalyst. The second step converts VCH to styrene via oxidative dehydrogenation using another proprietary tin/antimony oxide catalyst.

Develop a plant design for a world-scale 1 MMM lb/yr styrene process using the new Dow technology, and determine the overall economics.

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 safe to operate (e.g., no flammable or explosive mixtures).

Assume a U.S. Gulf Coast location. The BD contained in the crude C4 stream is valued at \$0.06/lb in 1997 dollars, and any remaining C4s may be returned to the ethylene plant at no cost. Styrene sells for \$0.30/lb. Oxygen may be purchased across the fence for \$0.02/lb.

References

Patent Watch, *Chemtech*, 20 (May 1995).

U.S. Patent 5,329,057, July 12, 1994.

A-IIS.7.3 Biodegradable PHBV Copolymer [PROC]
(Robert M. Busche, Bio-en-gene-er Associates, January 1995)

Because of the capacity limitations of urban landfills, biodegradable plastic packaging materials are of interest as a means to reduce the load on solid waste disposal systems.

Your research department has developed a mutant form of the bacterium *Alcaligenes eutropus* that expresses biodegradable poly (hydroxybutyrate) homopolymers and poly (hydroxybutyrate-valerate) copolymers. Although the copolymer has a lower melting point, it processes more easily than the homopolymer. As a result, both may have value in plastic packaging. Under optimum conditions both the homopolymer and copolymer are produced at volumetric productivities of about 1.0 g/L-hr. Both products are best produced under phosphate limitation. The copolymer is produced by adding *n*-propanol to the ethanol feed. The current research has been based on a fed-batch fermentation system. However, it has been proposed to use two-stage continuous culture in which the cells are first grown under conditions for optimum cell growth, followed by a second stage under conditions optimum for product accumulation. Your research department is eager to move ahead with the design of a commercial facility and will provide copies of appropriate references.

In the meantime, however, Dr. Douglas Dennis, an associate professor in the Biology Department of James Madison University, has cloned into a recombinant *E. coli* bacterium the genes that catalyze PHB formation in *Alcaligenes.* It appears that the new system produces polymer at the rate of 2.7 g/L-hr. He has offered to provide an exclusive license to Imperial Chemical Industries (ICI) and will consult on a plant based on the recombinant organism.

As head of the ICI corporate plans department, you have been asked to evaluate the commercial potential for developing a process to produce both homopolymers and copolymers at your plant at Atlas Point, south of Wilmington, Delaware. It is of interest to evaluate the economics of both a homopolymer and a copolymer product and to suggest an optimum split, if one exists. Your marketing department has suggested a combined capacity of 50 million pounds per year for the first plant. Either of the alternative processes could be considered.

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A-IIS.7.4 Xantham Biopolymer [PROC]

(Robert M. Busche, Bio-en-gene-er Associates, January 1986)

About 460 billion barrels of crude oil have been discovered in the United States to date, but only 120 billion barrels have been recovered by primary gas drives or secondary water floods. A large proportion of the remainder could be recovered, albeit at higher cost, by tertiary methods (enhanced oil recovery).

One such method involves the use of water-soluble polymers such as polyacrylamide to increase the relative viscosity of sweep water to that of the crude oil so as to promote the mobility of the residual oil in the reservoir. Polyacrylamide, although relatively cheap, does not possess the useful properties of polysaccharides such as xanthan gums, scleroglucan, dextran, etc. The biopolymers are injected at a rate of 1.4 to 1.7 lb/barrel of oil recovered. Excluding the polymer, the cost of the polymer/surfactant flood amounts to $30 nd $40/barrel, including capital charges.

Your company, a major oil producer, is concerned about the rapid decline in productivity of its Canyon Reef Reservoir in Kent County, Texas. Your Oil Production Department, which holds some patents on producing xanthan biopolymers, is considering forming a joint venture with a food company for developing and operating a fermentation facility to produce the 20 million annual pounds of polymer needed captively for a polymer flood of Canyon Reef. Merchant sales of xanthan for food uses by the partner would also be considered if economically desirable.

Your Research Department has confirmed that xanthan can be produced from glucose by the organism <italic>Xanthomonas campestris <roman>. Process and product data are summarized in the reports listed below.

Management has asked you to determine whether xanthan might be produced at a sufficiently low price to make the proposed EOR operation competitive with the importation of foreign crudes over the next decade. Your Senior Vice President has also asked whether selling xanthan for current food uses would help to launch the new business at an earlier date than that compatible with EOR market economics.

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A-IIS.8 ELECTRONIC MATERIALS

A-IIS.8.1 Silicon Wafers Through the Use of the Czochralski Growth Process [PROC] (Talid Sinno, University of Pennsylvania, January 2004)

Single crystal silicon is the dominant material for Very Large Scale Integrated (VLSI) and Ultra-Large Scale Integrated (ULSI) microelectronic device fabrication. Almost all single crystal silicon material is sold in the form of "wafers" or thin disks upon which microelectronic devices, such as computer CPUs and solid-state memory circuits, are built. The annual market for silicon wafers, which are typically produced in diameters ranging from 75 –300 mm, is about XXX billion and is expected to continue to grow as microelectronic device demand increases. Despite the immense market for single-crystal silicon wafers, only a few companies currently dominate the market. Examples of dominant players are Shinetsu Handotai in Japan, Wacker Siltronic in Germany, and MEMC in the USA. The goal of this study will be to assess the economic feasibility of entering the market for producing silicon wafers.

The production of single crystal silicon wafers is a multistep process summarized in Figure A-IIS.15 (taken from ref. [1]). So-called metallurgical grade silicon (MGS is 98% pure) is produced as a by-product of the steel industry.

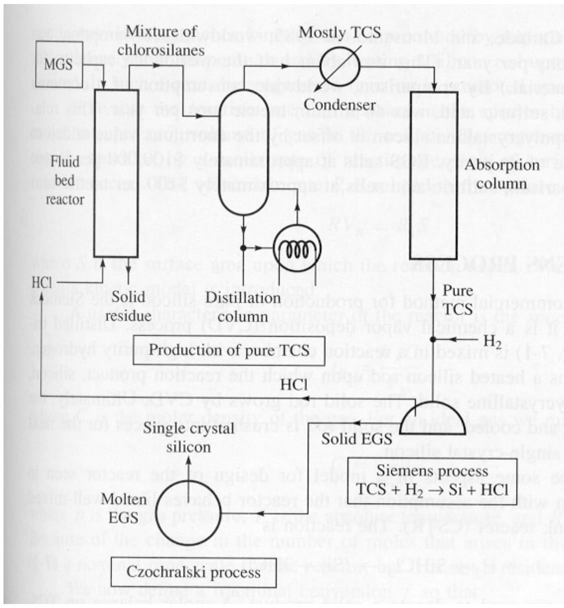

Figure A-IIS.15. Schematic representation of process steps in the production of single-crystal silicon wafers. Taken from ref. [1].

This material falls far short of the purity requirements for the device industry and must be converted to so-called electronic grade silicon (EGS). First, pure trichlorosilane (TCS: $SiHCl_3$) is produced reacting MGS with HCl at high temperature in a fluidized bed reactor. The vapor product stream from the reactor is then purified by distillation to extract pure TCS. The TCS is used to produce pure Si typically using the Siemens process, where TCS and hydrogen are reacted at high temperature.

The silicon is collected by deposition onto collector surfaces. This material, while pure, is a polycrystalline solid that is unsuitable for microelectronic device fabrication.

The final step of Si wafer production is the Czochralski (CZ) crystal growth process, in which pure polycrystalline Si is melted in a quartz crucible and then seeded with a small crystal to begin the single-crystal growth process, as shown schematically in Figure A-IIS.16.

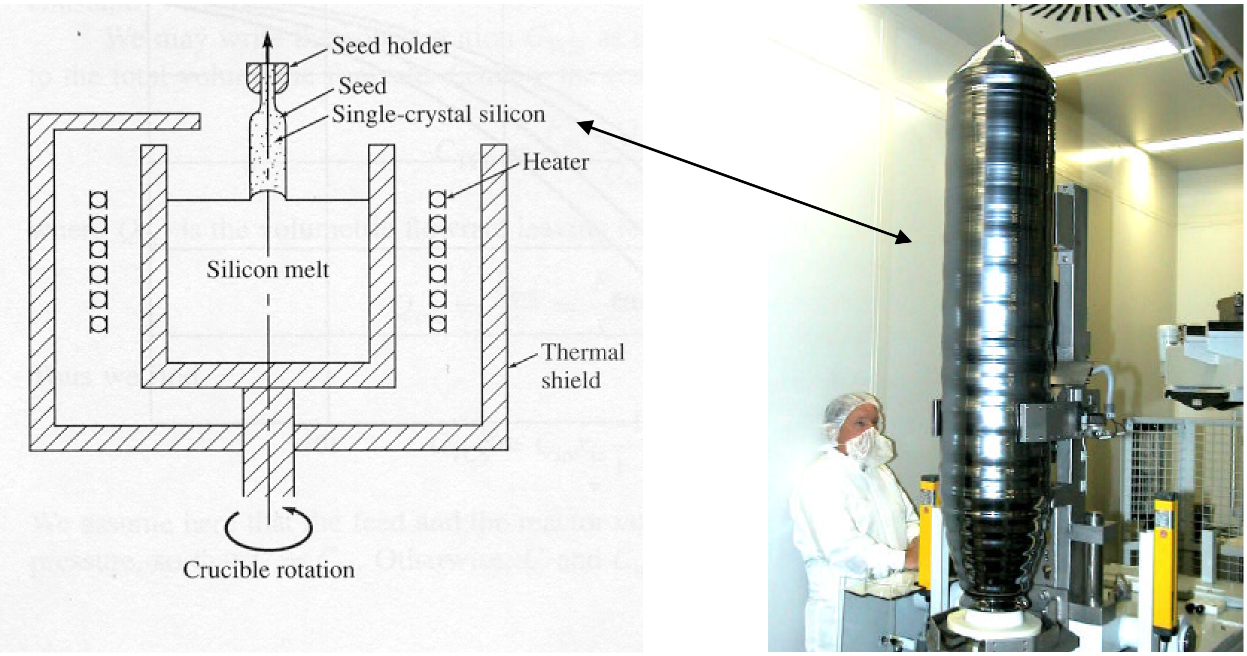

Figure A-IIS.16 (a) Schematic outline of the Czochralski crystal growth process for producing single-crystal silicon ingots. Taken from ref. [1]. (b) Actual 300 mm single crystal ingot grown at Wacker Siltronic.

Once the ingot has cooled it can then be removed from the crystal growth apparatus and sliced into circular wafers. The wafers are polished using a process known as chemical-mechanical polishing (CMP) and tested. Finally, they are packaging and shipped to customers.

Project Goals

Your goals for this project are described below. You will find that ref. [1] contains detailed discussions of the various processes discussed above and it is suggested that you begin your research for this project by reading the relevant sections (i.e., Chapter 7) in ref. [1]. In addition, ref. [1] contains many valuable citations that you may obtain either online or in print at the U. Penn library.

1. Perform a complete technical and economic analysis of the purification of MGS into EGS based on the Siemens process. Treat this phase of the project as would any other chemical process plant design. As shown in ref. [1], you do not need to consider the full reaction and transport details in the

Siemens reactor, but rather perform your analysis based on overall conversion and energy requirements.

2. Perform a detailed design and analysis, using the FEMLAB modeling software, of the Czochralski crystal growth process. The goal of your modeling efforts should be to estimate the heating requirements, and time needed to grow crystals of various radii and lengths. Note that the rate of crystal growth is an important limitation of your overall wafer production rate. In addition, you should provide design guidelines for the crystal growth process by performing sensitivity analyses of the appropriate parameters. As discussed in Chapter 7 of ref. [1], the CZ process is a highly complex process that involves a combination of heat and mass transfer, as well as fluid mechanics in the molten silicon container. Heat is transported throughout the system by a combination of convection, conduction, and radiation and all three processes usually are important.

You are to begin by constructing the simplest model possible in which only conduction and radiation are present – i.e. assume that the liquid melt does not flow. In addition, also begin by assuming that the crystal ingots are long and thin, so that the fin approximation can be used to simplify the modeling. Once this initial analysis is complete, you should consider more detailed (and more accurate) models as you see fit, given time and computer resource constraints.

3. Your final recommendations should be based on the assumption that you will need to build a completely new plant. Certain items such as CZ crystal growth units and ingot slicers, should be considered as "single-piece" items and priced accordingly.

References

1. Middleman, S., and A. K. Hochberg, *Process Engineering Analysis in Semiconductor Device Fabrication*, McGraw-Hill, New York, 1993.

2. Websites for major silicon wafer manufacturers:
   Wacker Siltronic: www.wacker.com
   MEMC: www.memc.com

3. Other sources of microelectronics-related information:
   International Sematech: www.sematech.org

A-IIS.8.2 Silicon-Germanium Heteroepitaxial Chips for Wireless Devices [PROC]

(Talid Sinno, University of Pennsylvania, January 2005)

While pure crystalline silicon wafers (which have a diamond lattice structure) remain as the most commonly used substrate for manufacturing microelectronic devices, other materials offer improved characteristics such as faster devices as well as light emission (i.e., lasers and light emitting diodes for solid state lighting), which silicon cannot. Examples of such materials are gallium arsenide (GaAs) and indium phosphide (InP) as well as silicon-based alloys such as silicon-germanium (SiGe) and silicon-carbide (SiC). However, the crystal growth of these materials is usually more difficult than pure silicon, particularly at the levels of crystalline perfection required for microelectronic device fabrication.

One possible approach for making some of these materials is to deposit a thin layer onto a perfect silicon substrate, which can be cheaply purchased from wafer manufacturers. This approach is particularly useful for the silicon alloys because they have the same lattice structure as pure silicon (diamond, or tetrahedral) and only differ in the lattice spacing.

The goal of this project is to design and analyze a reactor for depositing a layer of silicon-germanium alloy of a specified composition, i.e., $Si_{1-x}Ge_x$, onto a silicon wafer using an ultra-high vacuum chemical vapor deposition (UHVCVD) reactor which operates at a pressure of about 10^{-10} torr. The basic problem, however, is that the pure germanium lattice is about 4.2% larger than the silicon one. Thus, if one was to attempt to deposit pure Ge on pure Si, the Ge film would become unstable due to high stresses after about 4-5 atomic layers and would break apart. Given that the $Si_{1-x}Ge_x$ lattice spacing is almost linearly dependent on the Ge content, a possible approach is to vary the Ge content of the deposited film from $x = 0$ to the desired amount gradually in order to keep the stress from exceeding a critical value, where x is the mole fraction of Ge. This concept is shown schematically in Figure A-IIS.17.

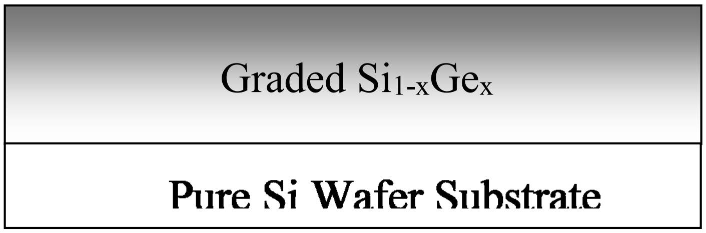

Figure A-IIS.17. Deposition of a compositionally graded layer of SiGe on a silicon substrate. Darker shade implies higher germanium content.

A schematic of an experimental UHVCVD reactor setup is shown in Figure A-IIS.18, based on the doctoral thesis of Middlebrooks (2001, University of Wisconsin), which is to be used as the basis for this project. The reactants are disilane (Si_2H_6) and germane (GeH_4) in hydrogen carrier gas. The disilane and germane decompose in a series of temperature-dependent surface reactions on the wafer surface to produce silicon and germanium atoms, respectively. The composition of the growing film is then controlled by the relative reaction rates as well as the relative inlet flow rates of disilane and germane.

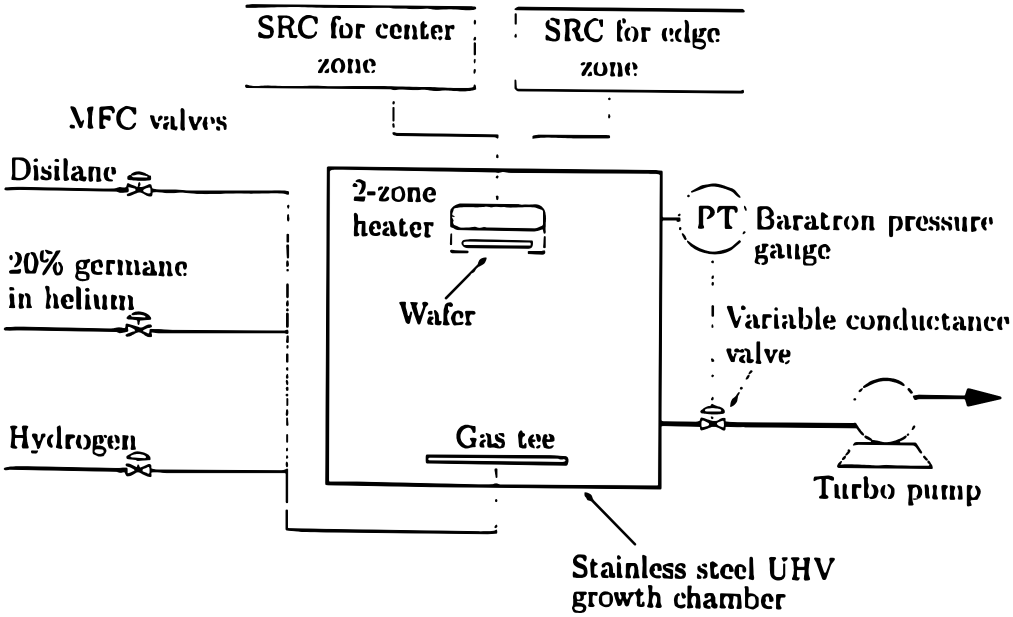

Figure A-IIS.18. Schematic of UHVCVD system for heteroepitaxial growth of SiGe films (Middlebrooks, 2001).

Kinetic Model for SiGe Deposition

A summary of the kinetic model in Middlebrooks (2001) is given here. Further details will be provided later as supplementary materials. All reactions represent surface reactions that take place on the wafer surface – gas phase reactions can be ignored due to the extremely low pressures in the system.

$$2Si_2H_6(g) + 6Si(s) \rightarrow 6SiH(s) + 2Si(b) \quad (1)$$
$$Si_2H_6(g) + 4Si(s) + 2Ge(s) \rightarrow 6SiH(s) + 2Ge(b) \quad (2)$$
$$Si_2H_6(g) + 5Si(s) + Ge(s) \rightarrow 6SiH(s) + Si(b) + Ge(b) \quad (3)$$
$$GeH_4(g) + 4Ge(s) \rightarrow 4GeH(s) + Ge(b) \quad (4)$$
$$GeH_4(g) + 3Si(s) + Ge(s) \rightarrow 2GeH(s) + 2SiH(s) + Si(b) \quad (5)$$
$$2SiH(s) \rightarrow 2Si(s) + H_2(g) \quad (6)$$
$$2GeH(s) \rightarrow 2Ge(s) + H_2(g) \quad (7)$$
$$SiH(s) + Ge(s) \longleftrightarrow Si(s) + GeH(s) \quad (8)$$

where (s) is a surface site, (g) is the gas phase, and (b) is a subsurface or bulk atoms. The latter is a product species. Reaction (8) is reversible and can be assumed to be at equilibrium. Temperature dependent rate constants for each of the above reactions will be provided once the project commences.

The total film growth rate is given by:

$$G = \frac{dh}{dt} = \frac{R_{Si(b)}}{\rho_{Si}} + \frac{R_{Ge(b)}}{\rho_{Ge}}$$

where ρ_{Si} and ρ_{Ge} are the atomic densities of Si and Ge, and $R_{Si(b)}$ and $R_{Ge(b)}$ are simply the production rates of Si and Ge. The time-dependent germanium mole fraction of the film; i.e., x in $Si_{1-x}Ge_x$, is given by the ratio of the production rates:

$$x = \frac{R_{Ge(b)}}{R_{Si(b)} + R_{Ge(b)}}$$

where the production rates can be derived using Eqs. (1)-(8). Other operating conditions such as the volumetric flow rates of the inlet gases, total reactor volume, reactor temperature, wafer temperature, and exit flow rate from the reactor, are parameters that need to be investigated as part of the design project, although guidelines will be provided based on the experimental system of Middlebrooks (2001).

Project Goals

Your goal is to design, model and optimize a UHVCVD reactor to deposit $Si_{1-x}Ge_x$, ($x = 50\%$) on purchased silicon wafers of varying diameters (200 mm and 300 mm diameter commercial wafers). The following issues should be considered:

1. You would like to minimize the film thickness to save time and money. The thinnest film possible is determined by how quickly you can change the composition to achieve the desired final composition. For the purposes of this project assume that films in which $dx/dz < 0.1\%/\text{nm}$ are stable. Note that the composition is a function of both the inlet flow rates of the reactants and the substrate temperature (because the rates of reaction depend differently on temperature).

2. The reactor model based upon Eqs. (1)-(8) is a set of ordinary differential equations that will be solved on a computer using software of your choice. A MATLAB/FEMLAB model is recommended.

3. The optimal operating conditions for growing compositionally graded films are obviously time-dependent. Some attention towards control of this system might be appropriate. The control variables are the inlet flow rates of the reactants as well as the wafer temperature.

4. In carrying out this design, it is important to set a reasonable production rate and estimate the installation costs and operating costs of the manufacturing train – i.e., the associated equipment. An estimate of the minimum price per heteroepitaxial wafer to achieve an investor's rate of return (IRR) of 20% should be determined.

A-IIS.8.3 Silicon Wafers for Photovoltaic Power [PROC]

(Talid Sinno, University of Pennsylvania, January 2006)

The photovoltaic (PV) solar energy market has exploded in the last decade and is expected to continue growing at an increasing rate in the near future due to international policy efforts such as the U.S. 1,000,000 and German 100,000 roof programs, as well as the current increases in oil prices and associated future uncertainty. The majority of PV modules in production today are based on silicon wafers in various forms (>90% of the total market) and there is strong current interest in further increasing the cost-efficiency of this technology to make it even more attractive. Almost every aspect of the production chain must be considered in this process, beginning with procurement of raw solar-grade (i.e. highly pure) silicon, fabrication of wafers, then functional solar cells, and finally the assembly into *modules*, which are the end commercial product (see Figure A-IIS.19). PV modules are packaged assemblies of multiple solar cells that are connected electrically and are ready to install on rooftops or in specially designated areas for commercial scale use. The ability to link as many or as few modules together make PV energy highly scalable and attractive for a wide range of uses.

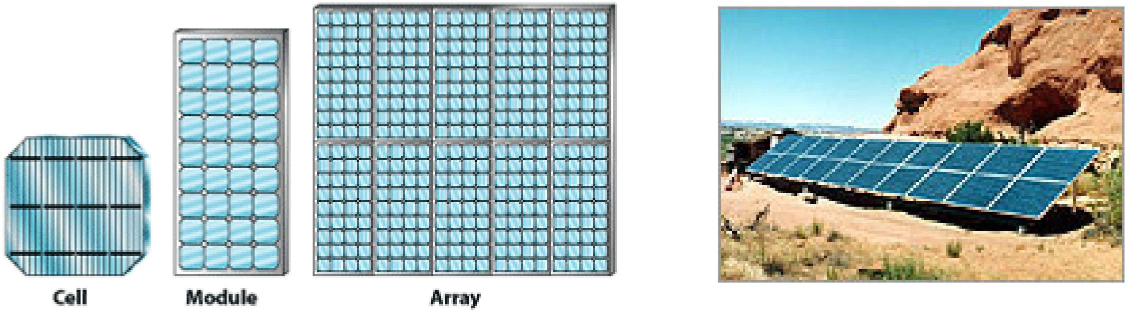

Figure A-IIS.19. From left to right – schematic figures of a solar cell (one wafer), module, and array. Rightmost figure is a photo of a solar array producing a peak power output of about 6.5 kW (Taken from DOE Website: http://www.eere.energy.gov/solar/silicon.html).

There are several fundamentally different approaches for producing silicon wafers appropriate for use in PV modules (as opposed to microelectronic use, which requires higher material perfection and purity). One class of methods begin with the melting of high purity polycrystalline silicon chunks ("polysilicon"), which are generally produced using a vapor deposition process known as the Siemens process (see the 2003 Senior Design Project of Cusack, Takizawa and Tam [ref. 1] for details). After melting the polysilicon in a crucible, the liquid silicon (T_m = 1,685 K) is resolidified to form either a single crystal (mono-crystalline silicon) or a polycrystal (multicrystalline silicon) solid. The latter material consists of many small crystallites of varying orientations separated by boundaries called *grain boundaries*.

Most monocrystalline silicon is produced using the Czochralski (CZ) crystal growth technique (described in detail in ref. [1]), which is also used to produce highly perfect material for microelectronic device fabrication. In the CZ process, a single crystal seed is dipped into a silicon melt and then slowly pulled out at a carefully controlled rate to grow a single crystal as shown in Figure A-IIS.20.

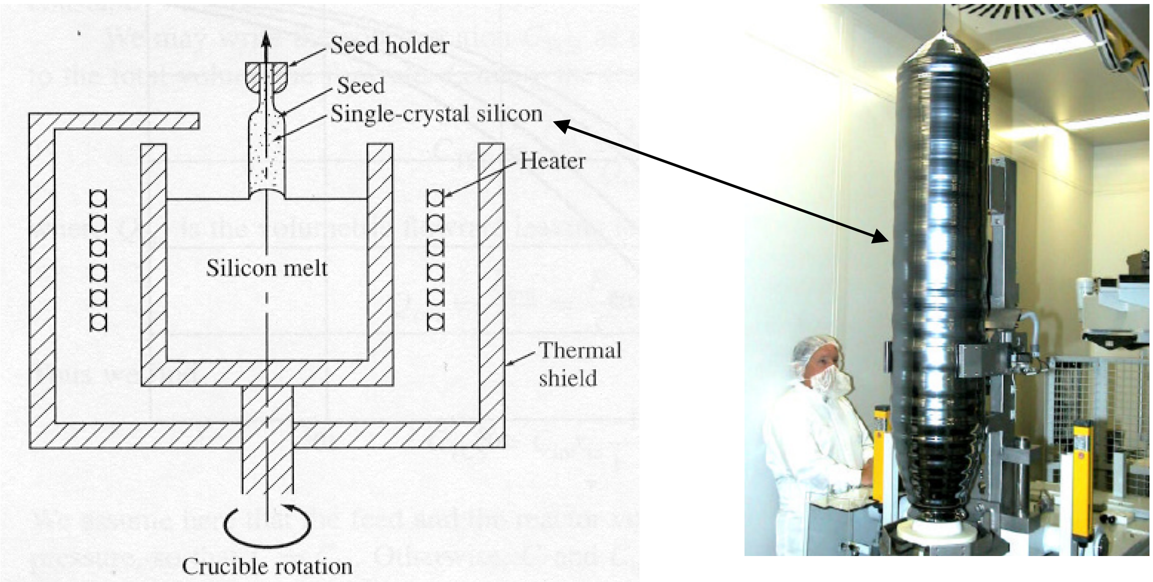

Figure A-IIS.20. (a) Schematic outline of the Czochralski crystal growth process for producing single-crystal silicon ingots. Taken from ref. [1]. (b) Actual 300 mm single crystal ingot grown at Wacker Siltronic.

The majority of multicrystalline silicon is produced by ingot casting (IC), in which a rectangular container is filled with molten silicon and then cooled until solidification is complete (see Figure A-IIS.21 for examples of ingot casting approaches in current use). The distribution of impurities, as well as the size of the crystal grains and number of other defects, depends on the cooling history in these processes. While slower cooling leads to better material, it also results in slower throughput and therefore increased costs.

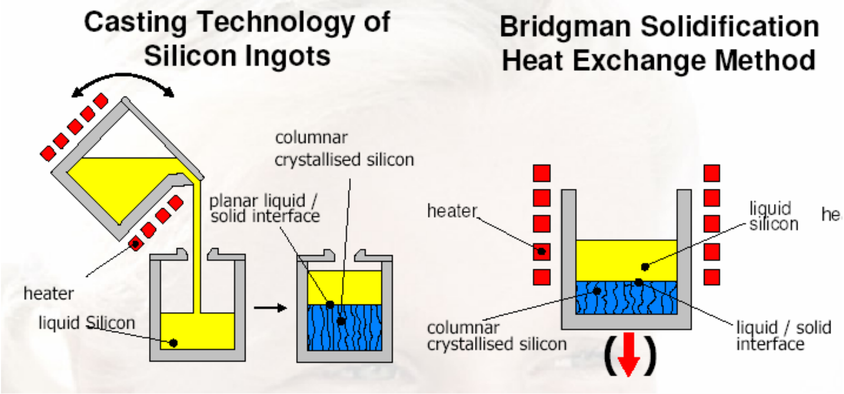

Figure A-IIS.21. Ingot casting of multicrystalline silicon (taken from ref. [2])

Recently, there has been increasing interest in an alternative class of methods for producing mutlicrystalline silicon wafers, known as Ribbon Growth-on Substrate (RGS) methods (Figure A-IIS-22). The advantages of the RGS approach is that it is (in principle) a continuous process, it does not waste silicon material (due to sawing of ingots), and therefore could be competitive with ingot casting approaches.

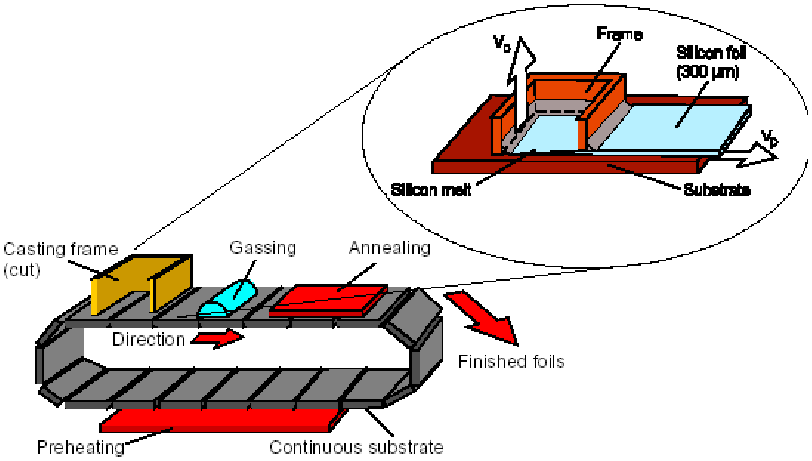

Figure A-IIS.22. RGS approach for growing silicon wafers [4].

Finally, another class of solar-cell fabrication methods, the so-called thin-film approaches, involve the deposition of silicon either from the vapor phase or from solution directly onto a substrate without the need for melt-processing. As shown in Figure A-IIS.23, thin-film approaches account for only a small part of the overall solar-cell market because they are not yet as well developed and will not be considered as part of this project. While RGS also currently represents a very small market share, it is increasingly likely that this will change soon as the process in Figure A-IIS.13 is refined further.

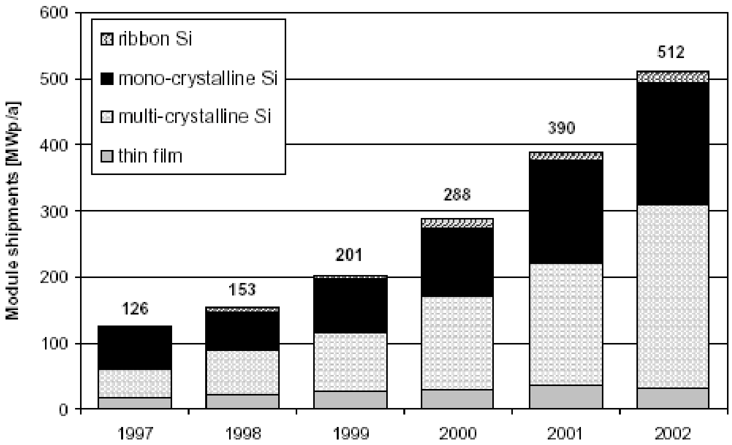

Figure A-IIS.23. World PV module shipments per technology. Taken from ref. [3].

One of the most critical metrics for determining how good a material is for PV applications is its efficiency (n), which is the fraction of impinging solar energy that can be converted into electricity.

The theoretical upper limit for silicon is about 30%, and currently the highest practical values attainable are between 10% and 25%, depending strongly on the wafer growth method. While lower-efficiency solar silicon is generally cheaper and faster to manufacture, the fixed costs associated with the rest of PV module assembly, as well as the desire to limit real estate requirements, make higher-efficiency material more attractive.

There are two major limitations to the solar efficiency of silicon: (1) crystal defects (grain boundaries and dislocations) and (2) impurities (mainly oxygen, carbon, and transition metals). The formation of crystal defects depends strongly on the growth method and in particular the cooling history of the material as it solidifies. In general, faster cooling leads to higher densities of defects but the absolute number is a complex function of the growth conditions. The impurity concentration is also closely related to the growth technique. For example, in both CZ and IC approaches, the crucible containing the silicon melt is lined with quartz, which dissolves during processing and introduces about 5-25 ppma oxygen impurity levels. Ref. [5] provides some information about the effects of impurities on solar cell efficiency. In general, the efficiency is a very complex function of these parameters and their interactions, but fortunately some empirical correlations exist in the literature which can be used to establish optimal process design guidelines.

Project Goals and Scope

The objective of this design project is to perform a technological and economic analysis of the currently available technologies for the production of silicon-based PV modules and propose a design for a PV module plant, including the production of solar silicon wafers. Your primary focus will be to consider the competing processes for producing solar silicon wafers, which contribute about 30-45% to the total cost of a PV module. In particular your aims will be to:

a. Analyze the heat transfer characteristics in the Ingot Casting, Czochralski, and Ribbon Growth processes using the FEMLAB software. In particular, you are to estimate feasible throughput rates as a function of equipment scale and operating conditions.

b. By performing an appropriate literature survey, find a way to empirically correlate the crystal quality (as defined by the number of defects and impurity concentration) to the growth conditions – these correlations will provide constraints on the allowable operating conditions for each process. Additional information on this aspect will be provided later. Pay special attention to the ingot casting approach because this technology is currently the most favorable for producing cost-effective solar silicon.

c. Using the results of your studies, design production plants for PV modules based on each of the various alternatives and perform an economic analysis for each. In addition to considering the solar silicon wafer fabrication methods outlined above, include analysis for the other steps required for making finished PV modules.

d. Current market demand for the raw polycrystalline material to make solar cells is so high that prices have been increasing and supply is limited. Investigate the economic feasability of building an on-site polysilicon manufacturing facility to reduce (or eliminate) the dependence on external sources for the polysilicon. You can use the design report in ref. [1] to guide you in this part of the project.

<u>References</u>

1. Cusack, S., E. Takizawa, and J. Tam, *Silicon Wafers Through the Use of the Czochralski Growth Process*. Senior Design Project in Chemical Engineering, 2003.

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   MEMC: www.memc.com
   DeutscheSolar: http://www.deutschesolar.de

A-IIS.8.4 Epitaxial Silicon Wafers by Chemical Vapor Deposition [PROC]

(Talid Sinno, University of Pennsylvania, January 2007)

A critical segment of the microelectronic device industry relies on the availability of so-called epitaxial silicon wafers. In these wafers, a thin layer of single crystal silicon is deposited onto a polished silicon wafer in order to provide a layer of extremely perfect crystalline silicon onto which microelectronic devices are fabricated. Although the substrate wafer is also almost perfectly crystalline and very pure, the epitaxial layer increases the level of perfection required for high value applications such as microprocessor chips (e.g., the recently introduced Intel Pentium Core 2 Duo chip). On the other hand, cheaper bare polished wafers (i.e., without the epitaxial film) are used in the fabrication of DRAM (Dynamic Random Access Memory) cells, which are much cheaper to fabricate per unit device area, and slightly lower yields are balanced by the cheaper wafer substrate.

Almost all of the commercial epitaxial deposition is carried out via the Chemical Vapor Deposition (CVD) process in which reactive gases are introduced into a deposition reactor at high temperature (typically around 1,000ºC). The gaseous reaction products are convected towards the silicon wafers by gas flow and then react with the bare silicon surface to form additional solid silicon layers. The quality of the silicon film is gauged primarily by its uniformity across the wafer diameter (the crystallinity is assured by the high temperature deposition conditions).

The goal of this project is to model, optimize, and compare several different reactor configurations for carrying out CVD of expitaxial silicon. There are many existing CVD reactor configurations suitable for silicon CVD, each of which balance energy requirements, deposition uniformity, and throughput. The polished silicon wafers (the feedstock for the deposition process) are readily available and can be purchased from crystal growth companies such as MEMC (USA) and Siltronic (Germany). Both 200mm and 300mm diameter polished silicon wafers can be purchased. Your aims will be to:

a. Using the scientific literature, find three reactor geometries that are suitable for epitaxial silicon CVD.

b. For each of these reactors, construct a COMSOL model to describe the reaction-diffusion-convection and heat transfer physics in the reactor chamber.

c. Using the COMSOL model, optimize the reactor to maximize throughput (i.e., deposition rate) while maintaining a minimum required uniformity of the deposited layer.

d. Compare the optimized reactors on the basis of a cost analysis and recommend an optimal solution.

You are to base your simulations on the gas-phase chemical models provided in ref. [1]. In the first chemical system, silane gas (SiH_4) decomposes into SiH_2 and H_2, which subsequently react to form a number of reactive radicals that react with the silicon wafer surface. If time permits, also consider the chlorosilane chemistry outlined in ref. [1] and determine if this chemistry is better than the silane one for epitaxial silicon deposition.

Examples of reactor geometries can be found in refs. [2,3], but you are not required to use these specific ones for your analysis.

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3. T. Setalvad et al., "Optimization of a Low Pressure Chemical Vapor Deposition Reactor for the Deposition of Thin Films", *Ind. Eng. Chem. Res.*, **28**, 1162 (1989).

A-IIS.8.5 Design and Control of Deposition Process using Microscopic Modeling [PROD]

(Talid Sinno, University of Pennsylvania, January 2008)

Thin film deposition technology is critical in a wide range of advanced materials processing applications including microelectronics, optics, and micro-electro-mechanical systems (MEMS). In many applications, thin films are generated by vapor deposition in which a vapor either condenses onto a substrate (physical vapor deposition or PVD) or reacts with the substrate (chemical vapor deposition or CVD). An example of a commercially important deposition process is the CVD of silicon on silicon wafers, in which a highly perfect layer of crystalline silicon is deposited on a silicon wafer surface to "bury" existing defects. This highly perfect *epitaxial* layer then serves as the substrate for fabricating microelectronic devices such as computer microprocessors.

The properties and quality of a deposited film depend strongly on the spatial uniformity, both in terms of the surface roughness, and in multicomponent systems, the chemical composition. As material requirements become ever more stringent, these quality metrics must be controlled to tighter specifications. A natural approach therefore is to seek avenues to control the reactor conditions (e.g. composition of the deposition flux and substrate temperature) during the deposition process.

In this project, you will develop a model for a deposition process and use it to design and test control strategies. You will use the work of Ni and Christofides [1] to guide you in developing the model and control strategy. A key issue is the fact that the controlled parameters, i.e. surface uniformity and composition, are **microscopic** quantities, which are not easily modeled using standard **macroscopic** models based on differential equations. To address this issue, you will construct a microscopic model based on the kinetic Monte Carlo (KMC) method. The KMC method is a stochastic approach in which atomic trajectories are generated by selecting individual atomic events, e.g. a move from one lattice site to another on a substrate surface. The probability of selecting a particular event depends on the rate of that event, i.e. fast events tend to get chosen more often. The rates of each type of event are usually tabulated in advance or calculated on the fly during the simulation, depending on computational efficiency and complexity of the problem.

The output of a KMC simulation is an atom-by-atom picture of the evolving deposited film, from which averaged properties such as overall surface roughness and compositional variation can be computed. Shown below in Fig. A-IIS.24 is a schematic representation of some of the different atomic events that are carried out in a KMC simulation [1].

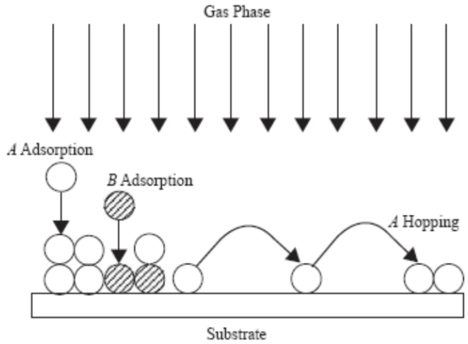


Figure A-IIS.24. Schematic representation of KMC atomic events on a substrate surface in a two-component system.

Your specific objectives in this project will be to accomplish the following:

a. Using the KMC modeling approach, build microscopic KMC models for the CVD process described in ref. [1]. Both single component and two-component models should be considered. Use the MATLAB environment to program the models. An example KMC code will be available to give you ideas on how to proceed.

b. Investigate the models parametrically to determine the effects of substrate temperature and deposition composition on surface uniformity and compositional fluctuations in the growing films. Also study the effects of the model parameters on the predictions. Example parameters include the interaction distance between atoms and the bonding energy between adjacent atoms [1].

c. Implement strategies using the KMC model to control surface uniformity and compositional variations to target values. Several control approaches are described in ref. [1] and related literature [2].

d. Discuss strategies to obtain optimal operating conditions. Generally, higher deposition fluxes lead to faster growth (lower cost of manufacture) but can compromise film properties. Using a parametric analysis, show how the maximum expected profit changes with assumptions on the capital expenses and selling cost/quality.

References

1. D. Ni. And P. D. Christofides, "Dynamics and Control of Thin Film Microstructure in a Complex Deposition Process", Chemical Engineering Science, **60**, 1603 (2005).

2. Y. Lou and P. D. Christofides, "Feedback control of Growth Rate and Surface Roughness in Thin Film Growth", AIChE Journal, **49**, 2099 (2003).

A-IIS.8.6 Design and Control using Stochastic Models of Deposition Reactors [PROD]

(Talid R. Sinno, Univ. of Pennsylvania, 2009)

Thin-film deposition technology is critical in a wide range of advanced materials processing applications including microelectronics, optics, and micro-electro-mechanical systems (MEMS). In many applications, thin films are generated by vapor deposition in which a vapor either condenses onto a substrate (physical vapor deposition or PVD) or reacts with the substrate (chemical vapor deposition or CVD). The properties and quality of a deposited film depend strongly on the spatial uniformity, both in terms of the surface roughness, and in multicomponent systems, the chemical composition. As material requirements become ever more stringent, these quality metrics must be controlled to tighter specifications. A natural approach therefore is to seek avenues to control the reactor conditions (e.g. composition of the deposition flux(es) and substrate temperature) during the deposition process.

A key issue is the fact that the controlled parameters, i.e. surface uniformity and composition, are **microscopic** quantities, which are not easily modeled using standard **macroscopic** models based on differential equations. To address this issue, you will apply a microscopic model based on the kinetic Monte Carlo (KMC) method. The KMC method is a stochastic approach in which atomic trajectories are generated by selecting individual atomic events, e.g., a move from one lattice site to another on a substrate surface. The probability of selecting a particular event depends on the rate of that event, i.e. fast events tend to get chosen more often. The output of a KMC simulation is an atom-by-atom picture of the evolving deposited film, from which averaged properties such as overall surface roughness and compositional variation can be computed. Shown below in Fig. A-IIS.25 is a schematic representation of some of the different atomic events that are carried out in a KMC simulation [1].

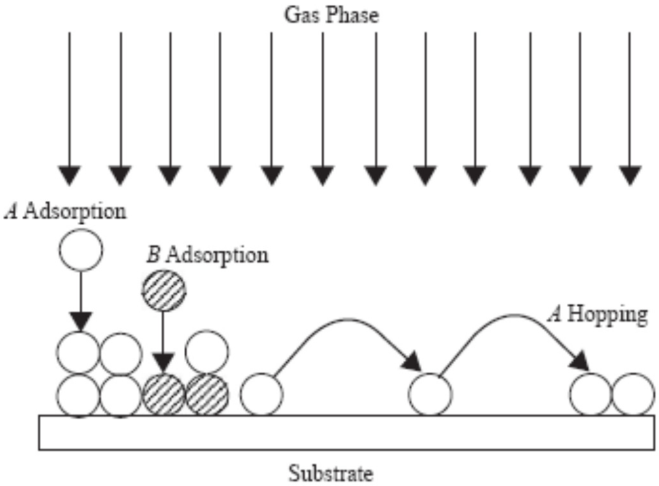


Figure A-IIS.25. Schematic representation of KMC atomic events on a substrate surface in a two-component system.

In this project, you will develop/extend a KMC model for a deposition process and use it to design and test control strategies. You will use the work of Ni and Christofides [1], and the 2007 Senior Design Project of Sahin, Uz, and Wallman (*Software Platform for the Simulation and Control of a Generic Deposition Process*) to guide you in developing the model and control strategy. The 2007 design project focused on a simple one-component deposition model and established the overall feasibility of this design and control approach. Your goal will be to extend this work to consider more detailed physical models, including multiple chemical components. Your specific objectives in this project will be to accomplish the following:

1. Using the KMC modeling approach, build and/or modify existing microscopic KMC models for the processes described in ref. [1] and the 2007 design report. Both single component and multiple-component models should be considered.

2. Investigate the models parametrically to determine the effects of substrate temperature and deposition composition on surface uniformity and compositional fluctuations in the growing films. Also study the effects of the model parameters on the predictions. Example parameters include the interaction distance between atoms and the bonding energy between adjacent atoms [1].

3. Implement strategies using the KMC model to control surface uniformity and compositional variations to target values. Several control approaches are described in ref. [1] and related literature [2].

4. Discuss strategies to obtain optimal operating conditions. Generally, higher deposition fluxes lead to faster growth (lower cost of manufacture) but can compromise film properties. Using a parametric analysis, show how the maximum expected profit changes with assumptions on the capital expenses and selling cost/quality.

References

1. D. Ni., and P. D. Christofides, "Dynamics and Control of Thin Film Microstructure in a Complex Deposition Process", *Chemical Engineering Science*, **60**, 1603 (2005).

2. Lou, Y., and P. D. Christofides, "Feedback control of Growth Rate and Surface Roughness in Thin Film Growth", *AIChE Journal*, **49**, 2099 (2003).

A-IIS.8.7 Design and Control Software for Materials Processing [PROD]

(Talid R. Sinno, Univ. of Pennsylvania, 2011)

Many materials processing technologies require careful control of features that are microscopic in nature and are not well described by continuum (i.e. field-based) models. An example is thin-film photovoltaic (PV) technology in which a thin layer of light-absorbing material is deposited onto a substrate. The advantages of thin-film PV over more traditional wafer-based silicon PV are now being realized as light-to-electricity conversion efficiencies become higher and processing technology improves, lowering cost. Examples of thin-film PV materials are Cadmium-Telluride (CdTe), Copper-Indium-Gallium-(di)Selenide (CIGS) [1], and silicon (Si) [2]. These materials are most often deposited onto glass or metal substrates, with typical film thicknesses being on the order of one to several microns. Controlled parameters of interest in such deposition processes are surface uniformity (i.e., roughness), porosity (void content), crystallinity (ordering extent), and chemical composition fluctuations (in multicomponent cases).

The goal of this design project is to utilize existing software for atomic simulation to develop a model for a deposition reactor that can be embedded into a model-based control (MPC) framework. The project will take advantage of the SPPARKS Monte-Carlo code (http://www.cs.sandia.gov/~sjplimp/spparks.html), which has been developed recently at the Sandia National Laboratory. This software allows the user to specify generic physical laws for describing the growth of a thin film onto an existing substrate. Shown in Fig. A-IIS.26 is a schematic representation of some of the different atomic events that are carried out in a deposition simulation [3].

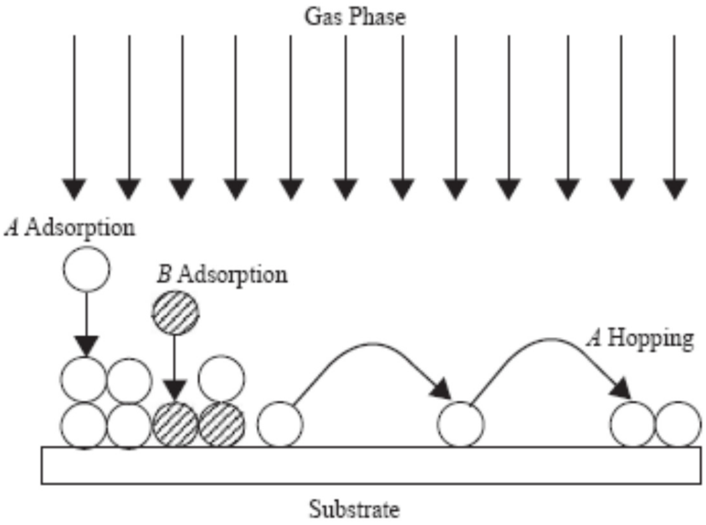
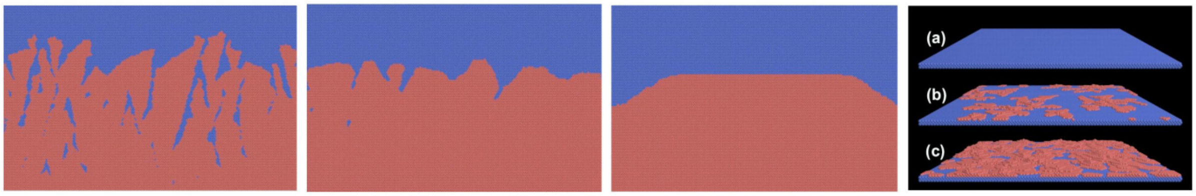


Figure A-IIS.26 Schematic representation of atomic events that can occur during a simulation of a generic deposition process involving two different chemical components.

Specific Aims of the Design Project:

1. In the first part of the project, you will construct simulations of a generic deposition process in order to familiarize yourself with the SPPARKS code. The goal here will be to develop a quantitative

understanding of how different process parameters such as temperature, deposition rate, and initial substrate texture affect the various deposited film properties, such as roughness, film porosity, and if possible, compositional distribution in a multicomponent system. Once these relationships are established you will use examples taken from the literature to build more realistic deposition models that correspond (approximately) to specific material systems; one example can be found in ref. [2], although others are readily available and can be considered instead. Example film configurations generated using the SPPARKS code for different deposition conditions are shown below for the specific case of crystalline nickel (taken from the SPPARKS website).



2. The second phase of the project will be to embed the SPPARKS code into a model-predictive control framework so that film parameters can be controlled dynamically during the growth of the film. The control algorithm will be implemented by writing a simple code (in a language such as C or Fortran, for example) that interfaces with the SPPARKS code via a script. The final product of the project will be an integrated piece of software, based on the SPPARKS engine, for modeling dynamically-controlled deposition processes.

3. Finally, using your software product, you will present a case study for an example deposition process in which the process parameters are optimized by balancing cost (generally specified by the throughput of your product) and film quality (which is dictated by the parameters specified above).

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1. M. A. Green, et al., “Crystalline silicon on glass (CSG) thin-film solar cell modules”, Solar Energy, **77**, 857 (2004).

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A-IIS.9 ENVIRONMENTAL – AIR QUALITY

A-IIS.9.1 F134a Refrigerant [PROC]

(John Wismer, Atochem North America, January 2001)

A major shift is occurring in the fluorochemicals industry, particularly in that part of the industry which manufactures refrigerants. This involves the shift away from chlorine containing CFC's (chlorofluorocarbons) and HCFC's (Hydrochlorofluorocarbons) to HFC's (Hydrofluorocarbons). This is because molecules containing chlorine degrade the protective ozone layer of the upper atmosphere. In automotive refrigerants, the shift has been away from R12 (Dichloro-difluoromethane) and towards R134a (1,1,1,2-tetrafluoroethane). This market is still growing as older air conditioning systems are phased out around the world. Refrigerants use a nomenclature which is universally accepted in the industry. A simplistic version involves the "rule of 90", in which 90 is added to the refrigerant's numeric code. In the resulting number, the last digit denotes the number of fluorine atoms, the second to the last, the number of hydrogen atoms, and the third from the last, the number of carbon atoms. When another digit occurs, it denotes the number of chlorine atoms. When the compound is unsaturated, an extra digit is added to the left to indicate the degree of saturation; "1" indicates a double bond in the molecule. The suffix letters denote the isomers based on symmetry considerations.

A major focus of the fluorochemicals industry has been to make use of retired HCFC or CFC manufacturing equipment in the manufacture of new refrigerants. This project involves Penn Refrigerants, a company with a fluorochemicals complex, which has several pieces of unused equipment, particularly for distillation. It has a significant infrastructure for handling emissions, including an aqueous acid neutralization system, an incinerator for liquid organic wastes containing acids, and a thermal oxidizer for combustion of gaseous wastes. In other words, small waste streams should not be a problem. It also has significant utilities infrastructure, including low temperature refrigeration (30 tons @ -40°C), a boiler plant capable of producing 150 psig steam with 20K lb/hr of unused capacity, an electrical substation which can supply both 460V and 220V 3-phase power, and a large excess of cooling tower capacity.

Penn Refrigerants is aware that there are several technologies available to manufacture F134a. They are considering licensing ICI's patented process. You (Quaker Consultants) have been approached to evaluate the capital required to retrofit the Penn Refrigerants plant on the Gulf Coast to make F134a using the ICI technology.

The ICI process is documented in U.S. Patent 5,382,722. It involves two reaction steps:

$$\text{TCE} + 3\text{HF} \rightarrow \text{F133a} + 2\text{HCl} \qquad (1)$$

$$\text{F133a} + \text{HF} \rightarrow \text{F134a} + \text{HCl} \qquad (2)$$

Not mentioned in the patent, but implied, is that gas phase reaction (2) has a relatively severe equilibrium limitation. Its heat of reaction is about 6.5 kcal/mol (i.e., endothermic) and the entropy of reaction is about -2.5 cal/mol-K. Also, the patent mentions a R1122 impurity which boils in the same range as F134a. This is the most troublesome olefin, but there may be others. One way to destroy these olefins is with chlorination technology. Penn Refrigerants has chlorine storage and feed systems available in their plant. Chlorination can be accomplished photochemically or perhaps, more simply, catalytically. The R134a molecule is resistant to chlorination at the temperatures used to saturate the double bond. The saturated chlorine-containing compound is much less volatile than F134a.

Penn Refrigerants has placed constraints on its plant:

> Gaseous HF or HCl cannot be compressed.
>
> HCl must be recovered by distillation and absorbed into aqueous form at 36% concentration.
>
> Inconel 600 or better is required for reactor and HF reboiler service

There are useful VLE data for mixtures of HF, F133a, and F134a in the *Journal of Fluorine Chemistry,* **61**, 123-131 (1993). Some LLE data are in European Patent No. 0 509 449 A2. Hydrogen fluoride has some odd thermodynamic characteristics which can make equipment design of HF systems tricky. A good guess at its enthalpy chart with a good discussion appears in a paper by Yarboff and Lightcap (*J. Chem. Eng. Data,* **9**, 2, 178, 1964). ASPEN PLUS uses a special equation of state to approximate the HF association effects. Does this approximation agree with the Yarboff and Lightcap chart? If not, how might this affect your design?

A listing of major equipment is as follows:

Off Sites
  Rail Car Unloading Station with ½ mi spur
  Aqueous HCl Storage
  Boiler Plant (20K lb/hr excess cap)
  Refrigeration at -40°C (30 ton)
  Cooling Towers - much excess capacity
  Waste Water Lagoon and Neutralization
  Liquid Waste Incinerator
  Thermal Oxidizer (Gaseous Waste)
  High Pressure Refrigerant Storage (400 psig) – 4 x 20,000 gal
  HF Storage - 4 x 20,000 gal
  Organic Feed Storage - 200,000 gal
  Chlorine Storage – 5,000 gal

Process Equipment:
  3 3 ft x 80 ft Distillation Cols. with Pall ring random packing (304SS)
    3 Condenser Systems – 3,000 ft^2, 1,000 ft^2, 600 ft^2; CS Shell/SS Tubes
    3 Reboiler Systems - all 150 ft^2; CS Shell/SS Tubes
  HF Feed Station (1 pump with in line spare; day tank)

Organic Feed Station (1 pump with in line spare, day tank)
Chlorine Feed Station (1 pump with in line spare)
  Chlorine Vaporizer (100 ft^2)
Aqueous HCl Storage - 300K gal

References

U.S. Patent 5,382,722.

Journal of Fluorine Chemistry, **61**, 123-131 (1993).

European Patent No. 0 509 449 A2.

Yarboff and Lightcap, *J. Chem. Eng. Data,* **9**, 2, 178 (1964).

A-IIS.9.2 Biocatalytic Desulfurization of Diesel Oil [PROC]
(Robert M. Busche, Bio-en-gene-er Associates, January 1994)

The EPA's revised pollution guidelines for on-highway diesel fuels took effect on October 1, 1993, and additional Clean Air Act amendments are pending. As a result, the sulfur content of diesel fuel will have to be reduced from 1 to 2% down to 0.05% as compared with 0.3% conventionally attainable with high-pressure hydrodesulfurization.

For a number of years researchers have attempted with little success to develop a biological system to remove organic sulfur. However, in 1989, J.J. Kilbane at the Institute of Gas Technology succeeded in isolating a bacterium that oxidized dibenzothiophene to 2-hydroxybiphenyl and liberated sulfur.

Based on this discovery, scientists at Energy Biosystems Corp. of Houston, TX, have been developing a biocatalytic desulfurization process using the bacterial enzyme IGTS8 to catalyze the reaction in a CSTR bioreactor. The extracellular enzyme is produced by the bacterium in an aerobic fermenter. The enzyme is then transferred as a supernatant solution to the bioreactor, where it mixes with high-sulfur diesel oil, oxygen, and other process chemicals. In the reactor, the sulfur is enzymatically removed from the oil to levels substantially below the 0.05% new regulatory limit without reducing fuel value. After reaction is completed, the water/oil emulsion is fed to a separator and the desulfurized oil is transferred to storage. The aqueous phase is sent to a separations unit to remove the sulfur, after which the enzyme/water mixture is recycled to the bioreactor after taking a purge of spent enzyme.

Dr. Daniel J. Monticello, VP Research for EBC, has recently invited your oil company to join a consortium to develop the process to the point of commercialization. Before deciding to accept this invitation, the director of your Refining Division has asked you to evaluate the expected economics of the proposed process as compared with the demonstrated costs for hydrodesulfurization in the 30,000-BPD diesel unit in your Richmond, CA, refinery. You are asked to identify the major cost elements and assess the sensitivity of cost to process improvements that might be effected with further research on economically critical process parameters.

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A-IIS.9.3 Sulfur Recovery Using Oxygen-Enriched Air [PROC]

(Mark R. Pillarella and Rakesh Agrawal, Air Products and Chemicals, January 1993)

The Clean Air Act, passed in 1990 and scheduled to become effective in 1995, will force chemical companies to reduce their emissions, into the atmosphere, of many environmentally detrimental chemicals. These include sulfur which occurs as H_2S in sour natural gas and refinery gas. Recognizing that sulfur recovery is a fast-growing business, you have recently formed your own engineering company, SULFREC, which specializes in sulfur recovery. A small chemical company has requested that SULFREC submit a bid to design a process for removal of sulfur from a 23-metric-ton-per-day gas stream (90 wt% H_2S and 10 wt% CO_2) using the modified Claus process described below. The principal reactions are:

$$H_2S + \tfrac{3}{2}O_2 \xrightarrow{\text{adiabatic flame temperature}} SO_2 + H_2O$$

$$2H_2S + SO_2 \xrightleftharpoons[\text{activated alumina}]{10^{\circ}\text{C above dew point}} 2S + 2H_2O$$

The H_2S - CO_2 gas is at 38°C and 1.72 bara. Ninety-five percent of the H_2S is converted to sulfur. The sulfur recovery system is to be installed in Houston, Texas.

The modified-Claus process typically uses air as its oxygen source. However, O_2 -enriched air may provide a more economical alternative. Your company has decided to investigate three alternative designs, each using the modified-Claus process, but with different oxygen sources:

1. Ambient air
2. O_2-enriched air using a membrane
3. O_2-enriched air using vacuum swing adsorption (VSA)

The company requesting the bid has stipulated that a comparison of the three alternatives, as well as a full design of the most economical process, be submitted.

Information on the modified-Claus process is available in the literature. Information for the design of the membrane and VSA processes will be supplied by Mark Pillarella at your request.

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A-IIS.9.4 California Smog Control [PROC]

(E. Robert Becker, Environex, January 1995)

Background

A primary gaseous air pollutant from combustion sources such as power plants is oxides of nitrogen (NO_x). Since NO_x is a known precursor to ozone formation, the Clean Air Act Amendments of 1990 call for reduction of NO_x from certain facilities throughout the United States.

You are a project engineer for an independent power producer in California. The state has mandated that your company reduce NO_x emissions from your Los Angeles facility by 200 tons per year.

The LA facility currently operates two units, a 25-MW combustion turbine and a set of four 3-MW (12 MW total) diesel engines. The diesel engines share a common exhaust stream. The NO_x reduction can come from either unit or both.

You are to design the NO_x removal system for each unit and determine which of the two systems is the most cost effective for NO_x removal.

The primary form of NO_x for a combustion source is nitric oxide (NO). The NO_x removal system to be considered is Selective Catalytic Reduction (SCR).

SCR System Background

SCR removes NO_x by reacting it with gaseous ammonia (NH_3) at about 700°F in the presence of a catalyst according to the reaction:

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

Kinetics

The rate of reaction is first order in NO_x and the overall apparent rate constant (combination of mass transfer and reaction rate) is 43,000 1/hr at 700°F.

A typical SCR system has four major components:

- A liquid ammonia storage tank
- An ammonia vaporizer
- An ammonia injection grid (to evenly disperse the NH_3 across the duct)
- A catalyst

The ammonia injection grid must be designed to evenly distribute the ammonia across the duct without restricting flow. Since NO concentrations vary across the duct, the ammonia injection grid must also be designed such that ammonia injection can be adjusted to match the NO concentrations across the duct of the exhaust system.

Several types of catalysts are used for SCR. The catalyst for this design is an extruded, square pitched homogeneous catalyst. A schematic of a catalyst brick is given in the figure.

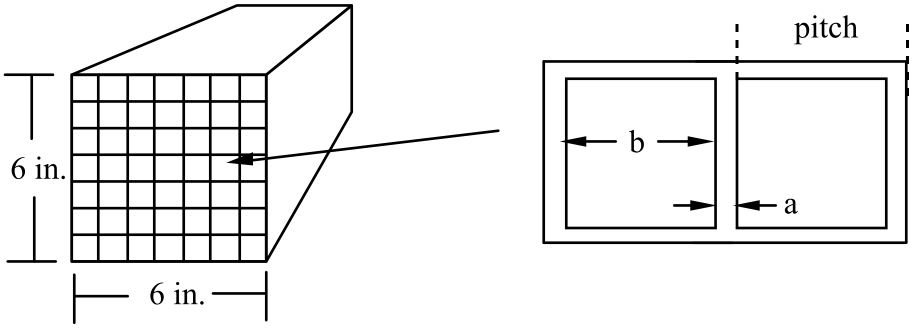

Figure A-IIS.27. SCR Catalyst Brick

The catalyst bricks are 6 by 6 inches and can be cut up to 3 feet in length. Catalyst bricks are then arranged side by side and front to back as necessary to achieve the desired dimensions.

The pressure drop over the catalyst is given by:

$$\Delta P = \frac{f\,L\,v^2 \rho}{4\,R}$$

where,

$$f = \frac{57\left(1 + 0.0445\left(\frac{2\,R}{L}\right)Re\right)^{0.5}}{Re}$$

Nomenclature

L	total length of the catalyst in the reactor (e.g. for 2 stacks of 3-ft-long bricks L = 6 ft)
a	wall thickness (see the figure)
b	open channel width (see the figure)
ε	voidage = $b^2/(b+a)^2$ (refer to the figure)
f	friction factor
ρ	gas density
R	hydraulic radius of catalyst channel (2 x channel cross section/wetted perimeter)
v	gas velocity in the catalyst channel
Re	Reynolds number

Design Specifications

Part of your assignment is to design the ammonia injection grid, catalyst and catalyst housing. Specify the number and arrangement of catalyst bricks and total catalyst volume. The ammonia injection grid is composed of a series of pipes with holes or nozzles to inject the NH_3. Keep in mind that the grid should be designed to evenly distribute the NH_3 across the duct and be flexible enough to adjust to match NO concentration variations.

Compare the cost of the two units to determine which is the economic choice. Compare both capital costs and NH_3 consumption over a 10-year catalyst life and the incremental cost on the power generated.

The turbine and engine specifications are as follows:

	Combustion Turbine	**Diesel Generator (1 of 4)**
Power Output	25 MW	3 MW
Fuel	Natural Gas	Diesel
Exhaust Flow	8,000,000 SCFH	600,000 SCFH
Engine Outlet Temperature	960°F	850°F
NO_x Emissions	150 ppm	2.0 g/kWhr
Max. Pressure Drop	5 in. H_2O	5 in. H_2O
Pressure Drop Cost	\$25,000/in. H_2O per yr	none

Anhydrous NH_3 Cost	170 \$/ton
Flue Gas Composition	
N_2	73.19 vol%
O_2	13.40 vol%
CO_2	3.40 vol%
H_2O	10 vol%
SO_2	10 ppmv
CO	25 ppmv
NO_x	as calculated

Catalyst Parameters	
Pitch	5.9 mm
Wall Thickness	1.0 mm
Catalyst Cost	300 \$/ft^3
Operating Temperature	700 ± 50°F

A-IIS.9.5 Zero Emissions [PROC]

(F. Miles Julian, DuPont, January 1991)

For many years your plant on the Texas Gulf Coast has produced tetrahydrofuran (THF) for use as a synthetic fiber intermediate. The reaction is carried out in water solution, producing a crude THF which also contains lower aliphatic alcohols as byproducts plus some gamma-butyrolactone (GBL), which is an unreacted intermediate. The THF is purified in a three-column distillation train. The impurities have been incinerated or sent with the water to the biological effluent treatment system.

Last week (without consulting the technical staff) your company's Board of Directors issued a press release stating that the plant is to be converted to a "Zero Emissions" operation by January 1, 1994. Your boss, the Chief Engineer, practically had a coronary on the spot, but he recovered in time to assign the job to your team. He also scheduled you to make a presentation to the Board of Directors on April 30, to outline your recommendations and present the economics of the various possible solutions. In practical terms your job is to reduce emissions to the lowest possible level, but to do it in the most cost-effective manner.

Some of the ground rules are:

- The three existing columns are not to be modified.
- Fluegas is considered to be an emission (greenhouse effect), so incineration is not acceptable.
- The cooling tower is not included in the Zero Emissions envelope.
- The biological treatment system is not an acceptable solution for the waste water.

If you can't burn it and can't discharge it, what can you do with it?

A local solvent supplier has offered to buy any of the alcohols which meet the purity specifications shown below. He has quoted the following prices for tank truck quantities:

99.8% Methanol	11¢/lb	99.5% Propanol	29¢/lb
99.7% Ethanol	29¢/lb	99.9% Butanol	54¢/lb

As an alternative, any mixture of alcohols can be sold as a gasoline additive for 9¢/lb, as long as it contains no more than 0.5% (wt) water.

THF can be recycled to the crude THF tank at an operating cost savings of 25¢/lb, and GBL can be recycled to an earlier step in the process at a savings of 15¢/lb. Any water and impurities which accompany these recycles must be reprocessed through the distillation train, but you may assume the existing columns can handle this.

Waste water can be used as cooling tower makeup, as long as its organic content is below 50 ppmw. It will replace raw water at a price of 35¢/Mgal.

The waste streams you must deal with are (lb/hr):

	Waste 1	**Waste 2**
Water	20,800	0
THF	11	83
GBL	385	0
Methanol	0	13
Ethanol	0	63
Propanol	361	90
Butanol	556	3

Binary activity coefficient data for these compounds are available.

The following utilities are available for your use:

150 psig steam, dry & saturated, @ $3.25 per Mlb.
50 psig steam, dry & saturated, @ $2.95 per Mlb.
Electricity @ 5.6¢/kWhr
Cooling Tower Water (30˚C) @ 5¢/Mgal

A-IIS.9.6 Volatile Organic Compound Abatement [PROC]
(E. Robert Becker, Environex, January 1994)

The 1990 Clean Air Act requires the reduction of volatile organic compound (VOC) emissions. All VOC emission sources of 10 tons/year or greater are required to retrofit abatement processes using the best available control technology (BACT).

A paint spraying plant emits VOCs from the vent of its paint spray booths. The stream contains primarily toluene, methyl ethyl ketone (MEK), and xylene, with small impurities of silicone and phosphorus. The concentration of VOCs in the dryer effluent varies between a minimum of 0.3 wt% VOC and a maximum of 1.2 wt% VOC with an approximate composition of 50% toluene, 25% MEK, and 25% xylene.

You are commissioned by the painting company to evaluate three alternative technologies for VOC reduction: thermal incineration, catalytic incineration, and carbon adsorption of the VOCs followed by destruction. A nearby bottle washing plant can use low-quality steam.

Design an emission control plant for 50,000 scfm of vent gas at 100°F and 25% relative humidity for 99% removal. The plant is located in Dearborn, Michigan, and the paint spray booths operate on a single 12-hour shift per day. Include the necessary start-up controls. The available fuel is natural gas or oil. Calculate the capital and operating cost and the $/lb or ton of VOC removed. Compare the three processes and recommend which is most suitable for this application.

A-IIS.9.7 Recovery and Purification of HFC by Distillation [PROC]
(Ralph N. Miller, DuPont, January 1997)

Your company, BIG-D CHEMICALS, is a major producer of pentafluoroethane (CF_3CHF_2), which is also known as hydrofluorocarbon 125 or HFC-125. HFC-125 is one of the new ozone-friendly fluorocarbons, and it is a replacement for chloropentafluoroethane (CF_3-$CClF_2$) or CFC-115 in many refrigerant applications.

In the production of HFC-125, some CFC-115 is produced, and this material must be removed from the HFC-125 product. In addition, hydrochloric acid (HCl) is always produced as a byproduct, and it must be recovered as a reasonably pure stream for the process to be attractive.

Your new job with BIG-D is to find the most economical process to recover HFC-125 from a mixture which contains HFC-125, HCl, and CFC-115. The HFC-125 product must contain no more than 100 ppm-wt of other organic impurities (e.g., CFC-115, HCFC-124, etc.) and the acidity level (as HCl) must not exceed 10 ppm-wt. In addition, the process will be more economically attractive if you can recover anhydrous HCl which contains no more than 10 ppm-wt of organic impurities. If you are unable to meet the anhydrous HCl purity specification, the HCl must be absorbed in water (35 wt%) and subsequently air stripped to remove the organic impurities. Aqueous HCl solutions are a drug on the market and have essentially no value; the absorption route is used only to avoid neutralization and waste disposal costs. Organics in the air stripper offgas must be collected and disposed of in an environmentally acceptable manner (e.g., incineration).

For the process to be economical, CFC-115 must be recovered and recycled to the reactor. Although recycle CFC-115 may contain up to 5 wt% HFC-125, there is a *cost penalty* associated with HFC-125 recycle, so you will probably want to minimize HFC-125 in the CFC-115 stream. The recycle CFC-115 may also contain up to 1 wt% HCl; there is *no* cost penalty associated with HCl recycle at this level.

The composition of the feed stream to the new recovery/purification process is: HFC-125 5,000 pph, CFC-115 500 pph, HCl 2,000 pph (available as a saturated vapor at 275 psig). The feedstock value of this stream is $2.50/lb.

The values of the various product and byproduct streams are as follows:

HFC-125 product (100 ppm organics, 10 ppm HCl)	$5.00/lb
HFC-125 in CFC-115 recycle	3.50/lb
Recycle CFC-115	2.50/lb
Anhydrous HCl (<10 ppm organics)	0.15/lb
Aqueous HCl (<100 ppm organics)	0.02/lb

The following utilities and services will be available as/when needed at the battery limits of the new purification facility. Costs are in 1997 dollars.

Cooling tower water	$0.09/1,000 gal	*1
150-psig steam	$5.00/1,000 lb	*1

50-psig steam	\$4.00/1,000 lb	*1
Cooling tower water	\$0.09/1,000 gal	*1
Raw water makeup	\$0.55/1,000 gal	*1
-25°C Refrigeration	\$0.12/hr/ton	*2
-45°C Refrigeration	\$0.20/hr/ton	*2
Electricity	\$0.065/kWhr	*1

*1 Includes allocated investment.
*2 Includes *electrical* costs for compressors and circulating pumps. Costs for required cooling water or allocated investment are *not* included. Compression requirements: -25 °C Refrig. = 2.4 Hp/ton; -45°C Refrig. = 3.6 Hp/ton.

BIG-D's fluorochemicals facility is located on the U.S. Gulf Coast. The new plant will be situated adjacent to an existing fluorochemicals manufacturing plant and will share some common facilities (i.e., control room, maintenance shops, technical office building, etc.). Storage facilities *exist* for both anhydrous and aqueous HCl. Except for the above, all equipment will be *new* (i.e., there is no used/existing equipment available for your use). You can assume an operating utility of 85% (7,446 hours per year) for both new and existing facilities.

CFC-115 (nbp = -39.1°C) and HFC-125 (nbp = -48.1°C) can be removed from HCl (nbp = -77.5°C) by *conventional* distillation; this process is energy intensive and requires low temperatures, but it has been *demonstrated* in the laboratory. BIG-D's research people have been very creative and have also developed an extractive distillation process for recovering HFC-125 and making high-purity anhydrous HCl. The extractive distillation process requires more equipment but uses less energy. Potential extractants are HCFC-123 (CF_3-$CHCl_2$), which is valued at \$3.00/lb, and HCFC-124 (CF_3-CHClF), which is valued at \$3.50/lb. These materials are available on site as pressurized liquids at 10°C and 100 psig.

Your assignment is to develop *both* conventional and extractive distillation processes for recovering HFC-125 and HCl from the specified feed mixture. You will need to develop optimum flow sheets, size and cost equipment for each case, and compare the economics of the two processes. Your flow sheets should include energy recovery (heat integration) as appropriate. You will also need to develop a control strategy for your preferred case; the control scheme should address start-up and shut-down conditions as well as steady-state operation.

Notes

1. CFC-115, HFC-125, and HCFCs 123 and 124 are nonflammable and noncorrosive. Carbon steel is a satisfactory material of construction for pressure vessels; if the temperature is less than 0°C (either operating or upset conditions), a Charpy impact test is required. HCl may be handled in either stainless steel or low-temperature carbon steel (Charpy impact tested) equipment.

2. On the U.S. Gulf Coast, cooling towers will *supply* water at about 31°C in the summertime. This should be the design basis for any water-cooled condensers or heat exchangers. The CTW supply temperature is about 10°C during the coldest months. CTW is high in chlorides (due to evaporation) and is quite corrosive.

3. The largest distillation column on the plant site is 150 ft tall. It was designed by the Plant Manager when he was a junior engineer a number of years ago. He is quite proud of this column, and he often points it out to new visitors to the site. You probably don't want to change this (or his feelings about you).

4. If any of the new process steps operate under vacuum, you should assume there will be air leakage into the process. While this is not a safety hazard, you will need to include facilities to remove inerts from the HFC-125 product.

5. Purity requirements for the new HFC products are much more stringent than for your current CFC products. As a result, analytical techniques have <italic>not yet been fully developed <roman>to analyze for low levels of some trace impurities. BIG-D's analytical chemists are currently working to develop more sensitive analytical methods to identify other impurities.

6. Thermodynamics/physical property information will be provided for the chemical species which are not available in your simulator's database.

Reference

"Process for Separating HCl and Halocarbons," U.S. Patent 5,421,964, assigned to E.I. DuPont de Nemours and Company, Wilmington, DE (June 6, 1995).

A-IIS.9.8 Carbon Dioxide Fixation by Microalgae for Mitigating the Greenhouse Effect [PROC]

(Robert M. Busche, Bio-en-gene-er Associates, January 1993)

Although reducing the concentration of carbon dioxide in the atmosphere and its concomitant greenhouse effect has become an increasingly important public issue, little progress has been made because the demand for electric power based on fossil fuels continues to grow. Worldwide, one-third of all carbon dioxide emissions come from electric generating plants. Emission levels can be lowered in one of three ways: (1) converting to alternative non-fossil fuels such as nuclear or biomass; (2) increasing the energy efficiency of the fossil fuel-based process; or (3) preventing carbon dioxide in the flue gas from reaching the atmosphere.

In Japan, Mitsubishi Heavy Industries, Ltd., and Tohoku Electric Company, Inc., have been experimenting with the use of microalgae to fix carbon dioxide in stack gas for subsequent recycle as a solid fuel. In this process, the algae, *Nannochloropsis salina* and *Phaeodactylum tricornutum*, are grown in sea water contained in shallow lagoons under an atmosphere of flue gas containing 10 to 12% carbon dioxide. The nutrients $NaNO_3$ for nitrogen and NaH_2PO_4 for phosphorus are added in small concentrations. After harvesting, the microalgae is dried and recycled to the power house as a solid fuel. The kinetics of the process were defined in the study.

As Branch Chief for the Department of Energy's Office of Carbon Dioxide Emission Control, you have been asked by the Deputy Secretary to evaluate the possible use of this approach in designing the emission control facilities for the proposed 600-megawatt generating station to be built between Los Angeles and San Diego to service the expanding needs of these communities. Government land can be made available for this purpose.

Specifically, you are asked to evaluate the cost and investment for an algae facility compared with the best alternative of your choice for reducing emissions by 50%. Alternative approaches to emission reduction are evaluated in the first four references. Your comments on the efficacy of other alternatives will also be of interest. Results should be expressed in terms of $/kWhr of generated electricity. Please test the sensitivity of cost to the levels of emission reduction for the approaches you consider.

Likewise, since the most effective way to reduce emissions is to increase the energy efficiency of the generation process, please ascertain the potential equivalent cost reduction vis-a-vis improvements in energy efficiency, and hence, determine the limiting minimum power cost at 100% efficiency. If data are available for the generation station under evaluation, determine the pertinent potential cost savings due to improvements in the energy efficiency.

<u>References</u>

Golomb, D., et al., “Feasibility, Modeling and Economics of Sequestering Power Plant CO_2 Emissions in the Deep Ocean,” MIT-EL 89-003 (December 1989).

Haggin, J., “Methods to Reduce CO_2 Emissions Appraised,” *C&E News*, 24 (September 21, 1992).

Herzog, H., E.M. Drake, and J.W. Tester, “Current Status and Future Directions of Sequestering Power Plant CO_2,” MIT, Cambridge, MA (1992).

Herzog, H., D. Golomb, and S. Zemba, “Feasibility, Modeling, and Economics of Sequestering Power Plant CO_2 Emissions in the Deep Ocean,” *Environ. Prog.* (February 1991).

Negoro, M., et al., “Carbon Dioxide Fixation by Microalgae Photosynthesis Using Actual Flue Gas Discharged from a Boiler,” 14th Symposium on Biotechnology for Fuels and Chemicals, Gatlinburg, TN (May 1992).

A-IIS.9.9 Hydrogen Generation for Reformulated Gasoline [PROC]

(E. Robert Becker, Environex, January 1994)

As a result of the Clean Air Act Amendments, hydrogen consumption within refineries will increase and hydrogen byproduct production from catalytic gasoline reforming will decrease. This increased use will be brought about by the required reduction of benzene, olefin, aromatics, and sulfur in gasoline and the reduction of aromatics and sulfur in diesel fuel. This demand will, in most cases, be met by on-site facilities for the production of hydrogen.

Hydrogen is currently produced by either steam reforming of methane or by partial oxidation of methane with high-purity oxygen and steam. Your research department has developed a new autocatalytic reactor using air, methane, and steam that has some very definite advantages. They are:

1. Refinery use will require high-purity hydrogen (99.9%) to minimize inert build-up in the recycle hydrogenation processes. In the autocatalytic process, the hydrogen separation is much easier than the nitrogen-oxygen separation and is less energy demanding than the reforming operation with steam.

2. The catalytic process operates at a lower temperature than is required for the steam reforming (1,000˚C as compared with 1,400˚C for the Shell/Texaco process). Moreover, the equipment is much simpler. The process can also be operated at higher pressures, thus saving on compression of the product hydrogen.

In the proposed process, methane, steam, and air are each preheated to 600-700˚C and fed into a catalytic reactor containing a bed of refractory nickel catalyst. Initial combustion results in a temperature up to 1,000˚C. The gas passes through heat exchange and a heat recovery boiler before entering a multi-stage CO shift converter. The gas then passes through a CO_2 wash tower to a cryogenic separation unit where the hydrogen is separated from the nitrogen, argon and methane.

You are required to prepare a preliminary cost estimate for a plant to produce 50 MM scfd 99.0% hydrogen at 30 atm. The following design data should be used for this evaluation.

H_2O/CH_4 feed ratio > 2.0 to prevent carbon formation

CO shift conversion is 99% of equilibrium.

Cost Data

Methane (100%) 30 atm	\$2.00/Mscf
Steam 30 atm satd.	\$6.00/1,000 lb
Power	\$0.07/kWhr
Cooling Water 90˚F	\$0.15/1,000 gal
Catalyst cost	\$10.00/kg

Economic Guidelines

Annual effective interest rate = 9%/yr
Project life = 10 yr
Minimum acceptable investor's rate of return (IRR) = 15%

Catalyst

The refractory nickel catalyst is a spherical pellet of 0.005 m diameter. The catalyst bed has a void fraction of 0.48 and a bulk density of 1200 kg/m^3. The catalyst must be replaced annually.

Kinetic Data

Rate of methane reacting (kmol/kg cat./hr) = $1.96 \times 10^7 \exp(-44{,}200/RT) \times P_M/(1 + 4P_H)^2$

where P_M = partial pressure of methane in bar
P_H = partial pressure of hydrogen in bar

The reaction on the catalyst is limited by the cracking reaction of methane, and the product gases (CH_4, CO, CO_2, H_2, H_2O) exist in near-equilibrium conditions.

A-IIS.9.10 R125 Refrigerant Manufacture [PROC]

(John Wismer, Atochem North America, January 2004)

A major shift is occurring in the fluorochemicals industry, particularly in the manufacture of refrigerants. This involves the move away from chlorine containing CFC's (chlorofluorocarbons) and HCFC's (hydrochlorofluorocarbons) in favor of HFC's (hydrofluorocarbons) because molecules containing chlorine degrade the protective ozone layer of the upper atmosphere. In commercial refrigerants, the shift has been away from R22 (Dichlorodifluoromethane) towards blends of HFC's. One of the most commercially important blend components is R125 (1,1,1,2,2-pentafluoroethane). Currently, Honeywell is the only large-scale R125 producer in the U.S, with additional capacity projected as the R22 phase-out continues.

Refrigerant nomenclature is universally accepted in the industry. A simplistic version involves the "rule of 90", which adds 90 to the refrigerant's numeric code. In the sum, the last digit denotes the number of fluorine atoms, the second to the last denotes the number of hydrogen atoms, and the third from the last denotes the number of carbon atoms. Any remaining atoms are chlorine. When the compound is unsaturated, an extra digit is added preceding the first digit to indicate the degree of saturation. Unity indicates a double bond in the molecule. The suffix letters denote isomers based on symmetry considerations.

A major focus of the fluorochemicals industry has been to use retired HCFC or CFC plants in the manufacture of new refrigerants. In this project, your company – Penn Engineering, has an existing infrastructure for fluorochemicals processing, including significant facilities for handling emissions, including an aqueous acid neutralization system, an incinerator for liquid organic wastes containing acids, and a thermal oxidizer for combustion of gaseous wastes. Using these facilities, small waste streams should be handled effectively. In addition, Penn Engineering has a significant utilities infrastructure, including low-temperature refrigeration (200 ton at -40°C), a boiler plant capable of producing 150 psig steam with 50 Klb/hr of unused capacity, an electrical substation which can supply both 460V and 220V 3-phase power, and a large excess of cooling tower capacity.

Your client is aware that several technologies are available to manufacture R125. Daikan, who has proposed a license or joint venture using their gas-phase technology, has approached them. Penn Engineering has been invited to evaluate the capital required to retrofit the plant on the Gulf Coast to make R125 using the Daikan reactor technology. The design capacity should be 50 MMlb/yr.

The Daikan process is documented in U.S. Patents 5,750,809 and 5,847,244, which refer to a two-step reaction path with the following estimated heats of reaction (which can be checked using bond-contribution estimates in ASPEN PLUS):

$$\begin{array}{lcll} CCl_2CCl_2 + 3HF & \rightarrow & CHCl_2CF_3 + 2HCl & \Delta H = -28 \text{ Kcal/mol} \\ \text{PERC} & & \text{R123} & \end{array}$$

$$\begin{array}{lcll} CHCl_2CF_3 + 2HF & \rightarrow & CHF_2CF_3 + 2HCl & \Delta H = -5 \text{ Kcal/mol} \\ \text{R123a} & & \text{R125a} & \end{array}$$

Quite often, gas-phase fluorocarbon reactions are equilibrium limited. You can check whether the Daikan reactions pose an equilibrium constraint by using bond-contribution estimates of free energies in ASPEN PLUS. If so, is there a way to relieve the equilibrium limitation? Although not mentioned in the patent, coking can be a problem with gas phase reactions that use olefinic feeds.

One of the major problems in F123 manufacture is the formation of F115, which is very difficult to separate from F125 by conventional distillation. Several patents document the removal of F115 by extractive distillation and selective hydrogenation, configured in a separation train.

In the Daikan process, the R110 series can be generated in several ways. One is by dismutation or disproportionation[11] of the F120 series. For example:

$$\underset{\text{R123}}{2\ CHCl_2CF_3} \rightarrow \underset{\text{R112}}{CCl_3CClF_2} + \underset{\text{R134a}}{CFH_2CF_3}$$

The dismutation reaction can be used as a proxy for all mechanisms that generate the R110 series. R112 successively fluorinates to R113 and R114 in the first reactor. In the second reactor, which fluorinates R123 to R125, any R113 and R114 fluorinates to R115. Of course, some dismutation can occur in the second reactor, but this is less likely as the R120 series becomes more fluorinated. Assume that R110 series selectivity is about 0.3% in the first reactor and about 0.1% in the second. Current specifications allow for 0.5 wt% F115 in F125. The other significant non-selective reaction can be dehydro halogenation of a saturated compound to an olefin. U.S. Patent 6,417,413 mentions R1111as a possible impurity. You can include a reaction to make R1111 at 0.2% selectivity.

Your client has placed three constraints on its plant:

1. Gaseous HF or HCl can not be compressed, and

2. HCl must be recovered by distillation and absorbed into water to achieve 36 wt% concentration.

3. In general, Inconel 600 or better is required for reactor and HF reboiler service.

Hydrogen fluoride has thermodynamic properties that can make equipment design of HF systems tricky. Yarboff and Lightcap[1] provide a good representation of the enthalpy chart, with a good exposition of the approximations and consequences. More recently, Visco[2] proposed an equation-of-state to represent HF thermodynamics and a method for predicting HF association in the presence of fluorocarbons[3]. Version 11 of ASPEN PLUS available to universities does not account for the enthalpy of association. Therefore, it is necessary to adjust the enthalpies to account for the enthalpy of association, using the Yarboff and Lightcap enthalpy chart, in unit operations that vaporizes HF.

Most of the hydrofluorochlorocarbons mixtures are nearly ideal. However, the liquid-phase activity coefficients of HF with most compounds differ significantly from unity, most of which are documented.[4,5,6] For binary pairs such as R125/HF, which do not have VLE data in the open literature, the following approximation should be satisfactory: (1) take VLE data involving a close analog like R134a[4] and regress it to get binary interaction coefficients, (2) use the binary interaction coefficients for HF/F125, and (3) check the HF/F125 data to confirm that an azeotrope exists near the value cited in the literature[10].

The ASPEN PLUS thermodynamic estimation methods are acceptable for simulating separation unit operations based on LLE and VLE data[4,5].

References

1. Yarboff, R.M., and E. H. Lightcap, "Thermodynamic Properties of HF", *J. Chem. Eng. Data*, **9**, 2, 178 (1964).
2. Visco, D., "Improved Thermodynamic Equation of State for Hydrogen Fluoride", *Ind. Eng. Chem. Res.*, **38**, 4125-4129 (1999)
3. Visco, D., "VLE/VLLE/LLE Predictions for Hydrogen Fluoride Mixtures Using an Improved Thermodynamic Equation of State," *Ind. Eng. Chem. Res.*, 41, 19, 4863-4872 (2002).

Equilibrium Data

4. Lee and Kim, "Vapor-Liquid Equilibria for Hydrogen Fluoride + Difluoromethane, 1,1,1,2-Tetrafluoroethane, and 1-Chloro-1,2,2,2-tetrafluoroethane at 283.3 and 298.2K", *J. Chem. Eng. Data*, **41**, 43-46 (1996).
5. Wilson, L., et al., "Vapor-Liquid and Liquid-Liquid Equilibrium Measurements on Twenty Two Binary Mixtures," *DIPPR Data Series*, **2**, 63-115 (1994); HF-123 is on p. 106.
6. Wilson, G., et al. (Wiltec Research), "Vapor-Liquid Equilibrium Measurements for the Hydrogen Fluoride/Hydrogen Chloride System," *AIChE Symp. Ser.* 81, 41-48, 1985.

Useful Patents

7. U.S. Patent 5,750,809 (Daikan) - Reactor Technology
8. U.S. Patent 5,898,088 (ICI) – Separation Train Technology
9. U.S. Patent 4,911,792 (Dupont) – Separation Train Technology and LLE data
10. US Patent 6,417,413 B1 (Honeywell)- Separation Train

Others

11. Lovelace, A.M., *Aliphatic Fluorine Compounds*, Reinhold Publishing, NY, p.46

A-IIS.9.11 Zero-Emissions Solar Power Plant [PROC]
(Adam Brostow, Air Products and Chemicals, January 2008)

Background

Figure A-IIS.16 shows a conventional solar power plant with solar collectors (concentrators). Heat transfer fluid in the primary circuit to the left (for example biphenyl-diphenyl oxide or a different type of oil) is heated in solar collectors and passed through the heat-recovery heat exchanger (HRHX), also known as the heat-recovery steam generator, to produce steam. Steam in the secondary circuit to the right is expanded in a turbine to generate power, condensed, and pumped back to the turbine inlet pressure (plus pressure drops in the circuit). This is a so-called Rankine cycle.

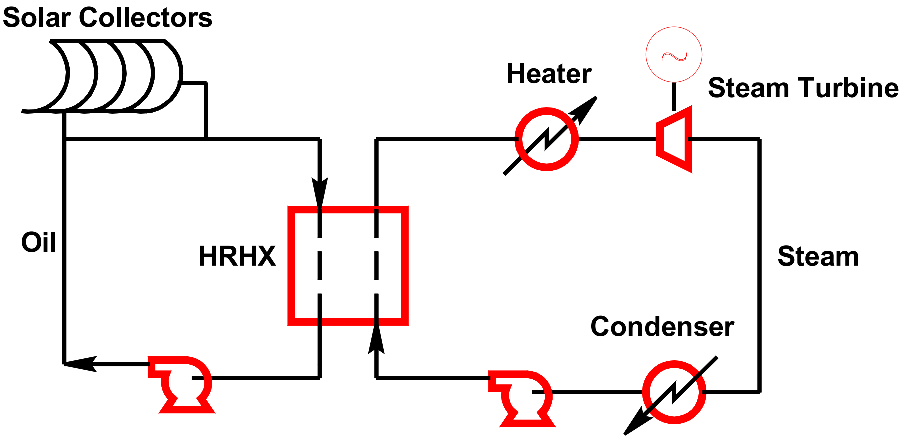

Figure A-IIS.28. Conventional solar power plant

The cycle typically uses an additional heater fired by fossil fuels such as natural gas. The heater is located on the steam circuit in parallel or in series with the heat-recovery exchanger (HRHX) and/or on the oil circuit. It supplements solar collectors and provides heat during periods of low solar radiation. The heater is the source of CO_2 emissions.

This technology was known for a quite a while. Because of increasing energy costs and environmental concerns, there is renewed interest in improving the concentrated solar power plants. There were several articles published this year, including in MIT's *Technology Review* and in the *New Scientist*. See the references.

A list of competing "zero-emissions" solar power technologies includes PVCs (photo voltaic cells). However, silicon production for the cells is energy-intensive (energy from fossil fuels) which offsets the benefits. PVC production also generates toxic PH_3, $POCl_2$, and HF emissions.

Another competing zero-emissions technology is direct steam generation (DSG) where the working fluid (such as water/steam) is directly heated in solar concentrators without the use of a heat-transfer fluid.

A centralized solar power facility uses several mirrors and one receptor. It may or may not use the heat transfer fluid.

An integrated solar combined cycle is a hybrid between a solar power plant and a conventional combined cycle.

Figure A-IIS.29 shows a conventional combined (Brayton/Rankine) cycle. Air is compressed in a compressor driven by a turbine and mixed with fuel such as natural gas. The gas is combusted; the resulting mixture is expanded in a turbine. This is so-called gas turbine. The still-hot exhaust from the turbine is used to generate steam and about 30% more power. New aero-derivative gas turbines with inter-cooling, for example Siemens LMS-100, are more efficient and have about the same exhaust temperature as the working temperature of a solar power plant (about 700°F).

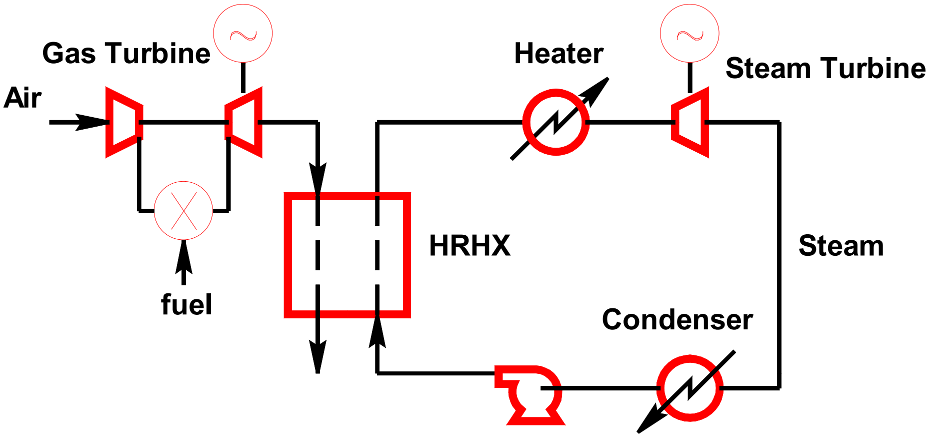

Figure A-IIS.29. Conventional combined cycle

Problem Statement

It is desired to design a zero-emissions solar power plant. The heat-transfer fluid (oil) will be heated to 390°C (734°F). The additional fossil-fuel fired heater will be eliminated. The working fluid will be heated and expanded to generate power.

Three working fluids will be considered:

- Water/steam
- A supercritical fluid such as CO_2, SO_2, NH_3, etc.
- Multicomponent mixture (if time permits).

Your design team is encouraged to find a way to store thermal energy during periods of low solar radiation.

As the first approximation, the steam turbine should be modeled as a single-stage turbine with up to 10% liquid in the discharge. When the percent liquid in the discharge is a bottleneck, it can be reduced by adding reheating units (multiple stream heat exchangers) and a second stage.

Another issue for a fixed flow rate of the working fluid (corresponding to the area occupied by solar collectors or the size of the centralized collector) is the inefficiency of latent heat exchange (water boils at constant temperature, and consequently, the cooling curves of the HRHX are far apart). A possible remedy is to use of a different heat transfer fluid that is supercritical on the high-pressure side of the cycle.

The process can be modeled in ASPEN PLUS using the MHEATX subroutine for the HRHX unit. It makes it easier to examine the cooling curves to assess the second-law losses as well as to model the reheat (multiple stream heat exchange). The solar collectors can be modeled using simple heaters (black boxes). A lost work (exergy) analysis can be performed to determine how much work can be extracted from the hot working fluid, as discussed in Chapter 9 (Seider et al.).

The economics should be evaluated for three different plant sizes: 10 MW, 50 MW, and 100 MW using equipment cost-scaling rules. The results should be compared against those for a conventional combined cycle. Carbon/CO_2 tax credits may influence the economics. Energy costs can be expressed in cents/KWhr. PVC power costs may also be included for comparison.

If time permits, you are also encouraged to model the conventional combined cycle with the combustion chamber (possibly using the RGIBBS subroutine in ASPEN PLUS) and look at the hybridization options.

You are encouraged to seek improvements based on the information you obtain, as well as brainstormed ideas, even if the problem statement is altered in scope.

References

"A Place in the Sun for Renewable Energy," *New Scientist*, 5 May, 2007.

"Solar Energy in Spain," *Technology Review*, September/October 2007
(involves centralized solar power)

"La Torre De luz," *Muy Interesante*, June 2007.

"Optimization Studies for Integrated Solar Combined Cycle Systems," ASME Forum, 2001

Integrated Solar Combined Cycle Systems

Solar Parabolic Trough (contains information about existing solar plants and compares different thermodynamic cycles.)

Links

General:
http://en.wikipedia.org/wiki/Solar_thermal_energy

http://en.wikipedia.org/wiki/Solar_power

Concentrated solar power (with PFD):
http://www.renewableenergyaccess.com/rea/news/story?id=43336

Concentrated solar power:
http://ec.europa.eu/research/energy/nn/nn_rt/nn_rt_cs/article_1114_en.htm

Solar plants in CA:
http://www.energy.ca.gov/siting/solar/index.html

A-IIS.9.12 Removing CO_2 from Stack Gas and Sequestration Technologies [PROC]

(William B. Retallick, Consultant, and Leonard A. Fabiano, University of Pennsylvania, January 2008)

CO_2 can be removed from stack gas by scrubbing with a water solution of monoethanolamine (MEA). To achieve this, the stack gas must be cooled to less than 100ºC.

An alternative is to use CaO, which adsorbs CO_2, but requires high temperatures for regeneration. Note that the partial pressure of CO_2 at equilibrium with $CaCO_3$ is 1 atm at 1,157 K. Whereas with $MgCO_3$, the partial pressure is 1 atm at just 700 K. Hence, one possible design concept is a cyclic process that avoids extreme temperatures. This could produce concentrated CO_2 that can be sequestered. The cyclic process would convert powdered MgO to powdered $MgCO_3$ reversibly. A challenge would be to keep this expensive fine powder from escaping.

Your plant will burn low sulfur coal and produce 500 MW of power. Your design will need to select a source of coal, and its composition, the efficiencies of the combustor/boiler to produce steam, and the efficiency to convert steam to electricity. You will also need to select the air/fuel ratio, presumably using excess air, the amount of flue gas to be generated and its composition. Given the amount and composition of the flue gas, you will seek to capture approximately 90% of the CO_2 generated for sequestration.

In summary, your design team will develop processes that involve the capture of CO_2 using MEA and MgO solutions, comparing their capital and operating costs. In addition, you team will study the options for CO_2 sequestration and determine the associated capital and operating costs. Finally, your team will select a method for sequestration and project its long-term effects on the environment.

References

Smith, R., "Inside Messy Reality of Cutting CO_2 Output," *Wall Street Jour.*, July 12, 2007.

Numerous references are available involving CO_2 recovery processes.

A-IIS.10 ENVIRONMENTAL – WATER TREATMENT

A-IIS.10.1 Effluent Remediation from Wafer Fabrication [PROC] (1993 Environmental Design Contest Problem)

It is required to design a plant to clean 15,000 gpd of the following waste stream from a wafer fabrication/computer manufacturing facility:

Cu	120 mg/L as Cu
Pb	20 mg/L as Pb
Sn	20 mg/L as Sn
Oil and grease	250 mg/L
Suspended solids (suspended copper, fiberglass, bentonite clay, etc.)	650 mg/L
Acids	
Fluoroacetic Acid	100 mg/L
Fluoroboric Acid	300 mg/L
Acetone	350 mg/L
EDTA	120 mg/L
Methyl Methacrylate	200 mg/L
Ammonium Hydroxide	200 mg/L
Formaldehyde	50 mg/L
Methanol	200 mg/L
Hardness	150 mg/L as $CaCO_3$

The treated effluent stream must satisfy the following limits:

COD = 300 mg/L
Cu = 2.7 mg/L
Pb = 0.4 mg/L
Sn = 1.0 mg/L
B = 1.0 mg/L
NH_4^+ = 20 mg/L as N

F = 5 mg/L
TOC = 130 mg/L
Oil and Grease = 30 mg/L
TSS = 200 mg/L
pH = 6-8
Total metals = 4.5 mg/L

where COD is chemical oxygen demand, TOC is total oxygen content, and TSS is total suspended solids.

There are no restrictions on the method(s) you select for remediation (e.g., physical, chemical, biochemical, leading, etc.). However, it is desirable not to generate much additional waste in the clean-up process. It is also desirable to find modifications that reduce the waste generation to levels that satisfy the effluent limits. Note that your company has sufficient capacity to store the contaminated stream for one month. Your design report should address health and regulatory issues.

A-IIS.10.2 Recovery of Germanium from Optical Fiber Manufacturing Effluents [PROC]

(Based on the AIChE Student Contest Problem, January 1991)

The manufacturing process for making optical fibers involves high temperature oxidation of silicon tetrachloride ($SiCl_4$) to form glass particles (SiO_2 and GeO_2) which are incorporated into a glass preform rod. This rod is subsequently drawn in a furnace to produce optical fiber. Germanium tetrachloride is added to increase the refractive index of the glass core in the optical fiber preform. It is known from experimental studies that the oxidation of $GeCl_4$ to GeO_2 proceeds to only 25% completion whereas oxidation of $SiCl_4$ is nearly complete. In addition, particle deposition is only 50% efficient, resulting in further losses of germanium. Due to this loss and the high cost of germanium, a need exists for developing a process to recover germanium from optical fiber manufacturing effluents. For environmental reasons, the process design must also provide for the removal of chlorine and particles.

Your company currently operates with 50 preform manufacturing units. Each unit is equipped with a small packed-column scrubber that is known to be underdesigned based on the current effluent production rates. The scrubbing solution is not recirculated and there is no recovery of germanium. Your engineering group has been designated to prepare a process design for a new scrubbing system to efficiently remove $GeCl_4$, Cl_2, and particles from the effluent stream:

$GeCl_4$	200 g/min
SiO_2	75
GeO_2	1
Cl_2	375
O_2	7

The new scrubbing system should remove 99% of both $GeCl_4$ and Cl_2. You should also design a system to recover germanium and convert it to $GeCl_4$.

In the existing process, vapors of $SiCl_4$ and $GeCl_4$ in an excess of oxygen are introduced into the optical fiber preform production units where the following reactions occur at high temperature:

$$SiCl_4 + O_2 = SiO_2 + 2Cl_2 \quad (1)$$

$$GeCl_4 + O_2 = GeO_2 + 2Cl_2 \quad (2)$$

Both reactions reach equilibrium which corresponds to 100% completion for reaction 1 and 25% completion for reaction 2. Incorporation of solid particles into the glass preform rod is only 50% efficient. The effluent stream therefore contains SiO_2 and GeO_2 particles, unreacted $GeCl_4$ and O_2, and the reaction product Cl_2.

Currently, effluents from each preform production unit are drawn into small (0.25 m diameter, 0.5 m high) packed bed scrubbers. The scrubbing liquid is an aqueous NaOH solution adjusted to pH 13. A single fan unit draws the effluents into the scrubbers. Due to operating requirements, it is not possible to make a tight seal between the effluent stream outlet and the inlet to the scrubbing system. Hence, the effluent stream gets diluted with a large amount of room air as it enters the scrubber.

Within the scrubbers, $GeCl_4$ and Cl_2 are removed from the gas stream by absorption and converted to soluble species according to the following reactions:

$$GeCl_4 + 5OH^- = HGeO_3^- + 4Cl^- + 2H_2O \quad (3)$$

$$Cl_2 + 2OH^- = ClO^- + Cl^- + H_2O \quad (4)$$

The particles dissolve according to:

$$GeO_2 + OH^- = HGeO_3^- \tag{5}$$

$$SiO_2 + OH^- = HSiO_3^- \tag{6}$$

Hydrogen peroxide (H_2O_2) is also added to the system to reduce the hypochlorite concentration according to:

$$ClO^- + H_2O_2 = Cl^- + H_2O + O_2 \tag{7}$$

The R&D department has found that germanate ($HGeO_3^-$) can be quantitatively removed from solution by precipitating with a divalent cation such as Mg^{2+} according to:

$$Mg^{2+} + HGeO_3^- = MgGeO_3^-(ppt) + H^+ \tag{8}$$

Similarly, silicate ions are precipitated according to:

$$Mg^{2+} + HSiO_3^- = MgSiO_3(ppt) + H^+ \tag{9}$$

Experiments have shown that $HGeO_3^-$ and $HSiO_3^-$ are precipitated equally well and that a mole ratio of 1.25 to 1 for Mg to total of Ge + Si is required to precipitate 100% of the Ge and Si. Mg can also be precipitated as $Mg(OH)_2$ according to:

$$Mg^{2+} + 2OH^- = Mg(OH)_2(ppt) \tag{10}$$

The R&D department has also measured the solubility of Ge and Si in scrubbing solutions at various pH values. The results are presented in a table (available from the AIChE) and may be useful in the design of a germanium recovery system.

$MgGeO_3$ can be used as a feed to make $GeCl_4$ which, after purification, can be used in optical fiber production. The tetrachloride is formed according to:

$$MgGeO_3 + 6HCl = GeCl_4 + MgCl_2 + 3H_2O \tag{11}$$

Additional reactions that may also take place include:

$$MgSiO_3 + 6HCl = SiCl_4 + MgCl_2 + 3H_2O \tag{12}$$

$$MgGeO_3 + 2HCl = GeO_2 + MgCl_2 + H_2O \tag{13}$$

$$MgSiO_3 + 2HCl = SiO_2 + MgCl_2 + H_2O \tag{14}$$

$$Mg(OH)_2 + 2HCl = MgCl_2 + 2H_2O \tag{15}$$

$$NaOH + HCl = NaCl + H_2O \tag{16}$$

These reactions are known to occur rapidly.

A-IIS.10.3 Solvent Waste Recovery [PROC]

(David G. R. Short, DuPont, January 1997)

Your company operates a polymer-processing facility which has three major waste streams. While there have been no major problems with the regulatory agencies in the past, the new CEO wants all facilities to have an environmentally friendly image. And there is a definite smell from your bio-pond which the neighbors complain about when the wind shifts. In addition, the existing permits are coming up for renewal. While the negotiations are seen as friendly, the expected outcome is to renew the current permit provided that an improved waste system is in place by the year 2002. The CEO thinks there is an economic incentive to have the facility running sooner.

Waste Streams

1. Air Stream: 40,000 scfm (60°F, 1 atm) air at 120°F, 2 psig. Contains 7 lb/hr acetaldehyde and 7 lb/hr methanol.

2. Water 1 stream: 100 gpm Water with 2 percent acetaldehyde.

3. Water 2 stream: 100 gpm water with 3 percent ethylene glycol.

Current Facilities

1. The air stream is vented to the atmosphere.

2. The water wastes are sent to a bio-pond. The waste chemicals are oxidized to CO_2 and H_2O. The pond is sparged with air to provide oxygen for the bacteria. The pond is at capacity. The holdup time for the complete oxidation of the wastes is 36 hours.

Specifications

1. > 90% removal of all contaminants from the waste streams. This includes any new vent streams which may be created in the waste facility.

2. If solvents are recovered for reuse, the purity must be at all times > 99.5% pure with water as the major impurity.

3. The waste-handling system must never shut down the production plant.

Upset Conditions

1. The air flow can decrease by as much as 50% in 30 seconds. The total contaminant load will stay the same.

2. The Water 1 stream has shown short-term flow rate fluctuations of 10% with no change in contaminant concentration.

3. The Water 2 stream has shown short term fluctuations of as much as 50% with a 2 × increase in the contaminant concentration.

Expansion Plans for the Polymer Facility

1. There is a high probability that the air stream will double in size, but the contaminants will increase by 50%.

2. The Water 1 stream will most likely have the same flow rate, but the concentration may be as high as 5% acetaldehyde.

3. The Water 2 stream will most likely double, but the concentration will be cut to 2% ethylene glycol.

Assignment

Design a facility that will meet the above specifications. Include in your study:

1. A discussion of alternatives to your final process.
2. A detailed development of your selected process.
3. A demonstration that the process is operable, using a model that shows the process can be started up, operated, and shut down.
4. A demonstration of the process sensitivity to changes in feed conditions.

A-IIS.11 ENVIRONMENTAL – SOIL TREATMENT

A-IIS.11.1 Phytoremediation of Lead-Contaminated Sites [PROC]

(Robert M. Busche, Bio-en-gene-er Associates, January 1995)

A large chemical company quartered on the East Coast spends about $400 million annually to remediate contaminated aquifiers and sites associated with past manufacturing operations. Much of this is spent on sites contaminated with lead from the manufacture of tetraethyl lead, lead-based paints, and lead cartridges. For example, the soil of a 25-acre site within a large plant located in New Jersey contains as much as 2,000 ppm of lead as inorganic salts to a depth of 2 feet. The distribution is as follows: at the surface, 2,000 ppm; 6”, 1,000 ppm; 12”, 500 ppm; 24”, 0 ppm.

A straightforward, albeit expensive way, to remediate this site would be to excavate the top 2 feet of soil and replace it with uncontaminated fill, then mix the contaminated material with cement to stabilize the lead, and dump it into a landfill. The cost of the remediation alone was estimated to amount to about $9 million. An additional $1.8 million would also be required for documentation, sampling, analytical tests, decontamination, etc.

Alternatively, Dr. Scott Cunningham, of Central Research's Environmental Remediation Services, has been experimenting with hyperaccumulating plants that can absorb lead and other heavy metals at up to 2% of the dry biomass weight. Such plants can produce 20 tons (dry basis) per acre per harvest of vegetative matter. Cunningham has identified as candidate crops a perennial plant, hemp dogbane, which yields a single annual crop, and two annual plants, brassica (Indian mustard) and common ragweed. Brassica can be planted in the spring and fall to yield two crops annually. Ragweed is planted in early summer and harvested in the fall before blooming. Operators involved in the planting, harvesting, and handling of the biomass are required to wear Level C personnel protective equipment (PPE), e.g., hooded, unlined Tyvek coveralls, goggles, and masks.

After harvest the biomass can be treated in a number of ways:

1. It can be incinerated to reduce its volume by 75%. The ash is then stabilized with cement and landfilled; or

2. It can be chopped, dried, and then fed pneumatically to a flame reactor as developed by the Horsehead Resource Development Company of Monaca, Pennsylvania. Natural gas and oxygen-enriched air (40 to 70% oxygen) are fed to the reactor with the biomass to produce a very hot reducing gas at 2,000°C. Under reducing conditions the biomass is consumed to produce carbon monoxide while the lead compounds are reduced to elemental lead *vapor*. Small amounts of biomass minerals and dirt from the harvest operation are melted into slag, which flows down into a horizontal separator where it is separated from the lead vapor. The nonhazardous slag is tapped, cooled, and disposed of in a landfill. The lead vapor is passed into a combustion chamber, where it is converted into the oxide, cooled with cold air, collected in a bag house, and stored. (It is extremely difficult and expensive to quench lead vapor without converting to the oxide.) The crude oxide is sold to a lead smelter at about 50% of the price for pure lead (currently 38 to 40 cents per pound); or

3. It can be chopped and fed with suitable nutrients to an anaerobic digester wherein 95% of the carbohydrate is converted to a mixture of carbon monoxide and carbon dioxide. In the process the lead precipitates as lead sulfide and is centrifuged to separate it from the residual carbohydrate and water. The aqueous layer is recycled to the digester after taking a suitable purge to bleed off salts. The aqueous waste can be treated with lime to precipitate the salts. As with alternative 2, the lead sulfide can be sold to a lead smelter at 50% of the price for pure lead.

As a member of your corporate plans department, you have been asked to evaluate the technoeconomic position of phytoremediation and recommend an appropriate plan of action for remediating the site to the plant manager. Cunningham has promised to provide additional information and, perhaps, a tour of his laboratory. John Pusateri of Horsehead will perhaps provide a tour of his pilot facilities.

References

Baker, A.J.M., and R.R. Brooks, "Terrestrial Higher Plants Which Hyperaccumulate Metallic Elements - A Review of Their Distribution, Ecology and Phytochemistry," *Biorecovery*, 81-126, Academic Publishers, Great Britain (1989).

Berti, W.R., and S.D. Cunningham, *Remediating Soil Lead with Green Plants*, Int'l. Conf. Soc. Environ. Geochem. and Health, New Orleans, LA (July 25-27, 1993).

Cunningham, S.C., and W.R. Berti, "Remediation of Contaminated Soils with Green Plants: An Overview," *In Vitro Cell. Dev. Biol.*, **29**, 207-212 (October 1993).

Farago, M.E., A.J. Clark, and M.J. Pitt, "The Chemistry of Plants Which Accumulate Metals," *Coord. Chem. Rev.*, **16**, 1-8 (1975).

A-IIS.11.2 Soil Remediation and Reclamation [PROC] (1993 Environmental Design Contest Problem)

A large area (hundreds of square miles) in an arid region of the Pacific Northwest has been contaminated with fallout from a neighboring manufacturing region. The site is to be both *remediated* and *reclaimed*. Remediation will be defined as reducing the concentration of identified contaminants below the threshold values listed below. Reclamation will include the use of a water harvesting system to enhance the growth of natural vegetation or agricultural crops on the site.

Water harvesting is an ancient concept that has been applied to increase biomass production in arid and semi-arid lands. Water harvesting concepts currently applied in arid lands continue to be somewhat primitive technically and small in scale. The desire to improve the technical state of water harvesting by finding, selecting, designing and/or testing sealants for catchment areas and by developing equipment that can apply the sealants on very large areas (hundreds of miles) in relatively short times (a few years) in a cost effective manner. These water harvesting catchments (sealed areas) may be tied into no drainage growing strips.

The design team is given the following three tasks:

1. Develop and demonstrate a bench scale process to remove the identified contaminants from a 5-kg sample of the soil. Develop a conceptual design of the process applicable to the field-scale project.

2. Develop and demonstrate a non-geomembrane, UV-resistant, water-repellent, erosion-resistant, sealant that can be applied to the soil surface as an aid in water harvesting.

3. Develop a conceptual design for a machine capable of applying the sealant developed in task 2 to the surface of the remediated area.

Regional and Soils Description

The area to be remediated is located adjacent to a large river in an arid climate. Natural vegetation is desert shrub and bunch grasses. Soil material is the result of catastrophic flooding followed by deposition of river alluvium. The resulting material is a mixture of cobbles and sandy loam soil material. The following particle size description is typical of the material at the remediation site.

SOIL

Component	Size (mm)	Weight Basis (%)	Weight Basis (%) < 2mm
Large cobbles	305	15	None
Small cobbles	152	30	None
Fine pebbles	8.5	5	None
Very course sand	2.000	10	20
Course sand	1.000	7	14
Medium sand	0.500	7	14
Fine sand	0.250	5	10

Very fine sand	0.106	4	8
Silt and clay	0.050	17	34
TOTAL		100	100

To approximate this material with a soil from New Mexico, we have chosen the soil series Casito (Petrocalcic Ustollic Paleargrid). This soil is formed in alluvium at the base of mountain watersheds. It is found on alluvial fans and terraces. It contains a similar mixture of cobbles and fines as the remediation site; however, the source of the alluvium is storm runoff rather than catastrophic flooding and river deposition. Provided below is some additional information on the contaminants in this soil.

Contaminants:

	Category	**Concentration per kg of soil**
1.	Pesticides, herbicides, insecticides	
	Lindane ($C_6H_6Cl_6$)	150 mg
	Methoxychlor ($Cl_3CCH\ (C_6H_4OCH_3)_2$)	150 mg
	Endrin ($C_{12}H_8OCl_6$)	150 mg
2.	Metals	
	Cadmium (Cd)	350 mg
	Silver (Ag)	100 mg
	Copper (Cu)	100 mg
3.	Organic Compounds	
	Ethyl Benzene ($C_6H_5C_2H_5$)	75 mg
	Methyl isobutyl ketone	
	$CH_3\text{-}CO\text{-}CH_2\text{-}CH\text{-}(CH_3)_2$	100 mg
4.	Halogenated compounds	
	Chloroethene (CH_2CHCl)	75 mg
	Tetra Chloroethylene (C_2Cl_4)	100 mg

The contamination is a surface type contamination (<1' deep) and must be removed to the levels:

1.	Pesticides, herbicides, insecticides	
	Lindane ($C_6H_6Cl_6$)	10 mg
	Methoxychlor ($Cl_3CCH\ (C_6H_4OCH_3)_2$)	10 mg
	Endrin ($C_{12}H_8OCl_6$)	10 mg
2.	Metals	
	Cadmium (Cd)	15 mg
	Silver (Ag)	15 mg
	Copper (Cu)	15 mg
3.	Organic compounds	
	Ethyl benzene ($C_6H_5C_2H_5$)	10 mg
	Methyl isobutyl ketone	
	$CH_3\text{-}CO\text{-}CH_2\text{-}CH\text{-}(CH_3)_2$	10 mg
4.	Halogenated compounds	
	Chloroethene (CH_2CHCl)	14 mg
	Tetrachloroethylene (C_2Cl_4)	14 mg

See the complete problem statement (1993 Environmental Design Contest Problem) which contains a detailed discussion of the tasks and the evaluation criteria.

A-IIS.12 ENVIRONMENTAL – RENEWABLE FUELS AND CHEMICALS

A-IIS.12.1 Fuel Processor for 5 KW PEM Fuel Cell Unit [PROC]

(Jianguo Xu and Rakesh Agrawal, Air Products and Chemicals, January 2002)

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:

	vol%
methane	95
ethane	2.0
propane	1.5
butane	0.65
pentane	0.35
nitrogen	0.5
organic sulfur	2 ppm

5 barg

References

Chemical Engineering, July 2001, pp. 37-41
AIChE Journal, July 2001, perspectives article.

A-IIS.12.2 Production of Low-Sulfur Diesel Fuel [PROC]

(Matthew J. Quale, Mobil Technology Company, January 2000)

There is a trend in recent environmental legislation to lower sulfur specifications in both gasoline and diesel fuels. You work for a refinery in the Delaware Valley that anticipates a new diesel specification requiring an order of magnitude lower sulfur than currently allowed. In fact, legislation is already in the works in Europe to lower the allowable sulfur to this new level by the year 2005. To achieve these low sulfur levels, you are to design a new catalytic hydro-desulfurization (HDS) system. This type of reactor has been in use in industry for a long time, but never for such severe service.

This unit will require just two feeds: a liquid feed blend from your refinery, and hydrogen. Since your refinery does not have a reforming unit (common hydrogen source within a refinery) or a hydrogen plant, you will have to buy the necessary hydrogen from a third party. Fortunately, a group similar to yours (1998/1999 Penn Senior Design Group – Khandker et al., 1999) recently designed a new hydrogen plant for the Delaware Valley that should be on-stream shortly before your unit and they are looking for new long-term supply agreements. Use the conclusions from their published report for information on the hydrogen purity and price. (I would recommend researching current contract hydrogen prices to ensure they are charging a reasonable price, however.)

Your R&D department has done substantial pilot plant work on this new process and has determined the following correlations to assist you in designing the HDS reactor. You also have processing data available from an older HDS unit within your company to use as a baseline.

Processing Conditions

A common value to track while designing a HDS unit is the percent hydrodesulfurization (%HDS):

$$\%\,\mathrm{HDS} = \left[1 - \frac{(\mathrm{wt\%\,S})_{product}}{(\mathrm{wt\%\,S})_{feed}}\right] \times 100\%$$

Different catalysts have different intrinsic activities, aging rates, and processing abilities/robustness. For your particular feedstock, the R&D department found the following correlations based on a reference catalyst. Terms denoted with a “$_0$” are the baseline data provided in Table A-IIS.3. The start-of-cycle (SOC) temperature is given by

$$\mathrm{T}_{SOC} = \mathrm{T}_0 + \mathrm{A} \times \ln\left(\frac{\mathrm{SV}}{\mathrm{SV}_0}\right) + \mathrm{B} \times \ln\left[\frac{\left(\dfrac{\mathrm{S}_{feed}}{\mathrm{S}_{product}} - 1\right)}{\left(\dfrac{\mathrm{S}_{feed}}{\mathrm{S}_{product}} - 1\right)_0}\right] - \mathrm{C} \times \ln\left[\frac{\mathrm{P}_{H_2}}{\left(\mathrm{P}_{H_2}\right)_0}\right] - \mathrm{D} \times \ln\left[\frac{\mathrm{H_2\ Circ.}}{\left(\mathrm{H_2\ Circ.}\right)_0}\right]$$

where T_{SOC} and T_0 are in °F. The aging rate is given by

$$AR = AR_0 \times \left[\frac{\left(P_{H_2}\right)_0}{P_{H_2}} \right]^E \times e^{F\left(\frac{1}{T_0} - \frac{1}{T_{SOC}}\right)}$$

where T_{SOC} and T_0 are in °R.

The values for constants (A – F) and the base and proposed operating parameters are given in the following tables. Please note that the equation and constants are Mobil Corporation internal numbers and should be cited as such.

Table A-IIS.2

Constant	**Value**
A	45
B	44
C	20
D	30
E	1.7
F	18,000

Table A-IIS.3

		Base Operation	**Proposed Operation**
Target Product Sulfur	wt%	0.05	0.005
Feed Sulfur	wt%	1.9	1.9
Reactor Conditions			
Feed Rate	TBD	35	35
SpaceVelocity (SV)	hr^{-1}	1.0	??
H_2 Circulation	scf/bbl	800	1,000 (min.)
H_2 Partial Pressure	psia	630	800 (min.)
SOC Temperature	°F	632	??
Aging Rate	°F/mo	4.7	??

The circulation and pressure values for the proposed operation are given as minimums to achieve the necessary product specifications. Increasing these values will improve the catalyst life, but result in higher capital and operating costs. It is left to you to determine the optimum values from an economic standpoint. To determine the catalyst cycle length, take 750°F as the maximum average bed temperature because higher values will produce product which has a color greater than ASTM 2.0 (the current spec).

Feed and catalyst information along with a brief overview of catalytic hydroprocessing (HDS in particular) will be presented to your group prior to beginning the project.

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A-IIS.12.3 Waste Fuel Upgrading to Acetone and Isopropanol [PROC]
(Robert Nedwick and Leonard A. Fabiano, ARCO Chemical, January 1997)

Your plant produces two byproduct streams from an existing process. Currently, these streams are being sent to the on-site steam boiler where they are burned to produce high-pressure steam for the complex. A recent change in the environmental regulations have put the major components of these streams (acetone and isopropanol) on an environmental listing, which will require you to spend capital to upgrade the existing boiler and storage tanks if you continue burning. You have been asked to determine the optimum disposition of these streams among the following options:

1. Continue burning these streams. The capital required to upgrade the boiler and storage tanks is $10.0 MM.

2. Build a unit to produce specification grade acetone product.

3. Pay to have the streams taken off site for proper disposal at the rate of 5.0¢/lb.

The following information is available:

Feed Composition and Quantity

Components, wt%	**Waste Acetone**	**Waste Isopropanol**
Acetone	80.0	12.0
Isopropanol (IPOH)	1.0	58.0
Methanol (MeOH)	10.0	7.0
Isobutylene ($iC_4^=$)	2.0	0.0
Methyl ethyl ketone (MEK)	0.5	0.0
Acetic acid	2.5	3.5
Heavies	1.0	1.5
Water (H_2O)	3.0	18.0
	100.0	100.0
Quantity, lb/hr	15,000	18,000
Heating Value, BTU/lb (water free)	12,000	12,000

Acetone Product Specification

Acetone	99.5 wt% min
Isopropanol (IPOH)	500 wt ppm max
Methanol (MeOH)	500 wt ppm max
Acetic Acid	50 wt ppm max
Water (H_2O)	0.5 wt% max

The isopropanol can be dehydrogenated to acetone per the referenced patents. The reaction is highly endothermic and at 90% conversion does result in coking of the catalyst, which requires a one-week regeneration burnout every two months. At 80% conversion, the catalyst run length can be extended to six months. Expected catalyst life is four regenerations after which the catalyst must be replaced at $6/lb.

Purification of the acetone product will require overcoming some azeotropes, acetone/methanol being the most important.

Your plant would be situated in an existing complex where much of the infrastructure is available.

The following is the situation with the Outside Battery Limit (OBL) components:

Site Development: Everything provided except:
- Site Clearing/Prep ($500M).
- Control Room Upgrade ($250M).

Utilities
- Firewater/N_2/Air/demineralized water/potable water are all available.
- Boilers are available to provide as much as 200 M lb/hr of 600-psig steam at $4.50/Mlb.
- Cooling Water is at its limit and a whole new system will be required.
- Electrical power is available at 4¢/kW.
- All utility and electrical tie-ins are required ($1,000 M).

Storage
- One fuel tank sized for the two waste fuels for 7days is available. (The acetone and IPOH streams are currently fed to a single tank before being sent to the boiler.)
- Product Storage for 14 days is required.
- Two Product Day Tanks for testing product quality before sending to the larger product tank are required.
- Any other new fuel, product, solvent, chemical, etc., storage associated with this process is required.
- Pipe runs from IBL to Storage and Loading areas are required ($500 M).
- Truck Loading upgrade is required ($350 M).

Environmental

- Waste water to the bio-pond can be treated for $2.00/Mgal.
- The flare system can handle 150,000 lb/hr extra load upon CW failure. If higher, an additional flare will be required.
- Tie-ins to these systems are required ($150 M).

Of the three options identified, only the acetone recovery has the potential for positive returns, but at the highest capital. The projected price of acetone is 25¢/lb in 2000, the target startup date for this unit. However, acetone has experienced large pricing swings being as low as 15¢/lb and as high as 30¢/lb for extended periods. Acetone is also a new product line for the company and there is some reluctance on management's part to get involved. Your company's philosophy is that a project must achieve a minimum economic hurdle rate of 12% investor's rate of return (IRR).

What do you recommend to your management?

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A-IIS.12.4 Conversion of Cheese Whey (Solid Waste) to Lactic Acid [PROC]
(Robert M. Busche, Bio-en-gene-er Associates, January 1993)

It is now January 1993, and the public is perceiving that the United States is burying itself in solid waste materials. ConAgra, Inc., has approached DuPont with a proposal for a joint venture to produce lactic acid for conversion to biodegradable polylactide plastics to be used in packaging and other markets that might help to alleviate the solid waste problem.

Under the proposal, the United States Ecological Chemical Products Company (Ecochem) will build a 20-million-pound acid plant based on cheese whey as a raw material at Adell, WI, where the Adell Whey Company will collect whey from producers within a 100-mile radius and supply it to the lactic acid plant via pipeline.

Key to the proposal appears to be the use of new technology being developed at the Oak Ridge National Laboratory under Dr. Brian Davison. The new process is based on a three-phase, biparticle, fluidized-bed bioreactor, in which lactic acid, produced continuously in a fluidized bed of immobilized *Lactobacillus delbreuckii*, is simultaneously adsorbed onto a solid polyvinylpyridine resin moving countercurrent to the fermenter beer. In this way, the pH can be maintained at the optimum 5.5 and product inhibition of the fermentation is minimized. As a result, fermentation rates have been increased 4- to 10-fold higher than the conventional fermentation process and the acid product can be recovered by methanol extraction.

As the Planning Manager for Chemicals, you have been asked to evaluate the techno-economics of the proposal as compared with the alternative conventional fermentation process and advise the Executive Committee of the financial expectations for the venture. It appears that if the design and financial evaluation can be completed by May 1993, the plant can be constructed for start-up in January 1996.

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A-IIS.12.5 Ethanol for Gasoline from Corn Syrup [PROC]
(Kamesh G. Venugopal, Air Products and Chemicals, January 1990)

In its environmental program, the Bush administration is evaluating clean-burning, low-volatile fuels for automobiles. One alternative is to convert a farm product, corn syrup, to motor-grade ethanol.

Your consulting company is requested to design a 100,000-metric tons/year, automobile-grade ethanol plant using corn syrup as the feedstock. After designing the process and determining its total cost, the price subsidy to make ethanol competitive with current gasoline prices should be determined.

In creating your design, give special consideration to processes that reduce the energy expenditure of the plant. In one such process, pervaporation membranes are used to dehydrate ethanol. Pervaporation is a membrane separation process in which the feed and residue streams are liquid, but the permeate is a vapor. The combination of permeation and evaporation in the membrane gives rise to separation factors much greater than can be accomplished by distillation and can be used to break azeotropes.

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A-IIS.12.6 Furfural and Methyl-tetrahydrofuran-based Biorefinery [PROC]
(John Wismer, Atochem North America, January 2006)

A growing number of experts are concerned that the recent increases in crude oil prices could presage the twilight of the age of oil[1]. The problem is that world demand keeps growing, but world production seems to be hitting a plateau. Current (2005) world consumption is about 84 million barrels per day (bpd), which is roughly in balance with world production. Much of the controversy about potential peak production surrounds the proven reserves and production capabilities of Saudi Arabia. The Saudis have been secretive about exploration and production data in recent years. Nonetheless, historical analyses of water injection rates into the major Saudi oil fields and past geological surveys are not encouraging[2]. Judging from the U.S. experience, once production rates peak, there will be a gradual decline over the next several decades.

With oil declining as a North American energy source, substitutes will come from three main sources sources: alternative fossil fuels (shale oil, coal, tar sands, natural gas), nuclear, or biomass. The recent publicity surrounding the hydrogen economy avoids the issue of the source of the energy, which would ultimately come from one of the above.

Biomass has always had the allure of being a renewable energy source. It has also been very controversial – in part because of the huge subsidy it enjoys through the excise tax forgiveness on motor fuels containing ethanol from biomass. Currently this subsidy amounts to $0.51/gal of ethanol, costing almost $2 billion per year as of 2004[4]. In addition, several states have subsidized capital for ethanol plant construction and passed laws mandating its use in the gasoline pool. Much of the criticism of this program concerns the alleged negative energy balance incurred in ethanol production; that is, that more energy is expended in growing, harvesting, transporting, and processing the raw material than is recovered in the form of ethanol[5]. The basis of this argument is that ethanol can never be competitive because as the cost of energy increases, ethanol processing costs increase as well. Ethanol proponents claim that increases in crop yields and process improvements have already overcome the negative energy balance. These arguments arouse skepticism in that they are made in support of keeping the ethanol subsidy, not phasing it out.

Most of the ethanol produced from biomass comes from the fermentation of glucose contained in corn starch. Lignocellulosic biomass is another potential glucose source and has been the focus of much research in recent years. It is very plentiful in the form of timber and agricultural residues. The glucose in cellulose is polymerized in a form more difficult to ferment than starch-based material. Cellulose purity is another problem. Lignocellulosic biomass has three major components: cellulose, hemicellulose, and lignin. Cellulose is predominantly polymeric hexose (mostly glucose), hemicellulose is primarily pentosans or polymeric pentose (mostly xylose), and lignin is polymeric phenyl propane. Functionally, cellulose is the plant's fibrous material, while lignin is the glue holding the fiber together. The pulping process in paper manufacture is a delignification process. Many researchers have focused on enzymatic conversion of the cellulosic pulp to ethanol. One of the big problems is that the pentosans in hemicellulose are hard to ferment and produce a five-carbon cyclic aldehyde called furfural, which can inhibit fermentation. In the interest of producing ethanol and its subsidy, researchers have done creative work to co-ferment the two sugars. Much research funding is now targeted toward developing a "biorefinery", a plant that processes all of the lignocellulosic biomass into fuels and useful chemicals[3]. For the most part, thus far, the production of ethanol has been the goal of biorefinery concepts proposed.

A biorefinery that focuses on converting biomass pentosans to furfural, as a precursor to liquid fuels, appears in many ways to be superior to the ethanol-based concept. Whether or not the energy balance around ethanol is positive or negative, production of ethanol is clearly an inefficient vehicle for recovery of solar energy. The glucose molecule contains five energy-laden carbon-carbon bonds. In fermentation, the glucose molecule is converted to two molecules of ethanol and two molecules of CO_2, and consequently, only two of the five carbon-carbon bonds are recovered as a source of energy in ethanol. By contrast, the reaction to make furfural retains all of the carbon-carbon bonds of the pentose, recovering more of its inherent energy value.

Furfural is produced by first hydrolyzing the pentosans to pentose, then dehydrating the pentose. Furfural production from biomass feedstocks is not new. Quaker Oats made furfural from oat hulls, sugar cane bagasse, and rice hulls for years until the 1990's. However, they shut down their plants as their process became relatively inefficient. Currently, most of the furfural consumed in the U.S. is imported from China, South Africa, and the Dominican Republic. One problem of the Quaker Oats process was its low yield based on pentose, because furfural forms non-selective compounds by reaction with xylose. In countries where the research funding is not skewed towards the production of ethanol, improvements on this process have been a priority. Researchers at the University of Tokyo have proposed a pervaporative membrane reactor to remove furfural as it is formed[11]. In addition, a group in South Africa has proposed a process in which the furfural is flashed into the vapor phase as it is formed[12,13]. Both groups claim yields of furfural close to 100% based on pentose. Like ethanol, furfural forms a binary azeotrope with water (65 wt% water). However, unlike ethanol, the azeotrope is partially immiscible with water, and consequently, it can be broken by liquid phase separation.

The U.S. consumption of furfural is only about 40 million lb/yr. Currently, a new market in agriculture, as an environmentally-friendly nematicide, is being created. For the large volumes of furfural produced by a biorefinery, however, it is assumed that conversion to a motor fuel additive would be required. Furfural cannot be used directly as a motor fuel because it forms acid too readily. However, a patented process[17] by the Pure Energy Corporation hydrogenates furfural to 2-Methyltetrahydrofurwn (2-MTHF), which has been approved by the DOE as an additive for fleet vehicle fuels[16]. Water is condensed off as a by-product in the reaction. Like furfural, water forms a heterogeneous azeotrope (at 10 wt%) with 2-MTHF, which can be broken by liquid phase separation. 2-MTHF has the potential to become a high-value fuel additive. It is partially oxygenated, giving it a high octane rating, and is cyclic, giving it a low vapor pressure relative to the other C5 species. Furthermore, it can act as a co-solvent for alcohols such as ethanol and methanol with gasoline.

Integration of 2-MTHF production into a biorefinery can be accomplished in one of two ways. First, the biomass can be processed directly to furfural with the lignin and cellulose residues separated afterwards[14]. A problem with this approach is the difficulty in removing the furfural from the lignocellulosic residues. The separation process can cause non-selective reactions and cellulose degradation. Alternatively, a new pulping technology, patented and marketed by PureVision, which claims to separate the cellulose, hemicellulose, and lignin components of biomass[9], can be used. It apparently can work on any cellulosic feedstock. The cellulosic portion could be used to make ethanol, but is perhaps more valuable as a high quality pulp[10]. The hemicellulose portion is fed to the chemical process that makes furfural and then MTHF. The lignin portion is isolated and sold as a clean heavy fuel. One challenge in this process is heat integration. A large excess of hot water is used in the biomass fractionation. Heat recovery would be an essential part of any design.

Your task is to evaluate the furfural-based biorefinery concept. You will need to select the capacity, with fuel additive plants usually large. However, you will need to be sure that your feedstock can be supplied all year. This can be a problem in biomass processing where feedstock availability tends to be seasonal. However, the PureVision pulping process appears to allow for any feedstock. So sugarcane bagasse or rice hulls (high hemicellulose contents) could be used in season, with wood chips used at any time. In this regard, you will need to demonstrate the heat and material balance with a couple of feedstocks. Also, because biomass contains much water, the transportation cost of the feedstock needs to be addressed. Furthermore, although the biomass feed can be assumed to be a residue, it has an opportunity cost. Most pulpers and food processors have installed equipment to recover fuel value from these residues, and consequently, it should be assumed to have the value of a low cost fuel. It is reasonable to assume that, given its unique properties, 2-MTHF will enjoy a premium over gasoline exceeding that realized by the defunct MTBE octane booster.

Some qualitative comparison with competitive biorefinery concepts is needed to sell the concept to both investors and the DOE, which would be expected to provide funding for process development and possibly a demonstration plant. Any economic evaluation must take into account the steadily increasing oil prices that would be anticipated if oil production has indeed peaked.

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A-IIS.12.7 Furfural and THF in China – Corn to Clothes [PROC]

(Gary Sawyer, Lyondell Corporation, January 2007)

Polytetramethylene Ether Glycol (PTMEG), the major component of spandex fibers, is made by polymerizing tetrahydrofuran (THF). THF can be produced from a variety of starting materials, most commonly from 1,4-butanediol, which in turn can be produced from propylene oxide and syngas, butane, or acetylene and methanol. An earlier process involves extracting furfural from agricultural wastes, then hydrogenating furfural to THF. This process is gaining renewed attention as bio-based chemical feedstocks begin to compete with high-cost crude feedstocks. China, in particular, has maintained a furfural industry and is currently the world leader in its production.

Your engineering firm has been selected to design a process for the production of THF from corn cobs in the agricultural regions of China. The corn cobs have zero value and no disposal costs where the corn is processed, but the THF plant must cover their transportation costs. You should design large-scale plant, requiring corn cobs from a large region, which will be transported using hopper trucks. Note that the price of THF varies with the cost of more traditional (crude oil) based feedstocks, as shown in Table A-IIS.1.

Your deliverables will include:

1. A process design, with heat and material balances, equipment list, and disposition of waste streams, for a 50-150 kTA THF plant. You should explain your choice of plant scale; that is, THF production rate.

2. A cost estimate to build the plant.

3. An expected *return on investment* (ROI) depending on the THF value. At what cost of crude oil would you expect corn-based THF to be competitive at 15% ROI?

Furfural is made from the acid hydrolysis of pentosan, which is found in corn cobs, rice and oat hulls, almond husks, other food wastes, and various woods. The chemistry of pentosan to THF is outlined below:

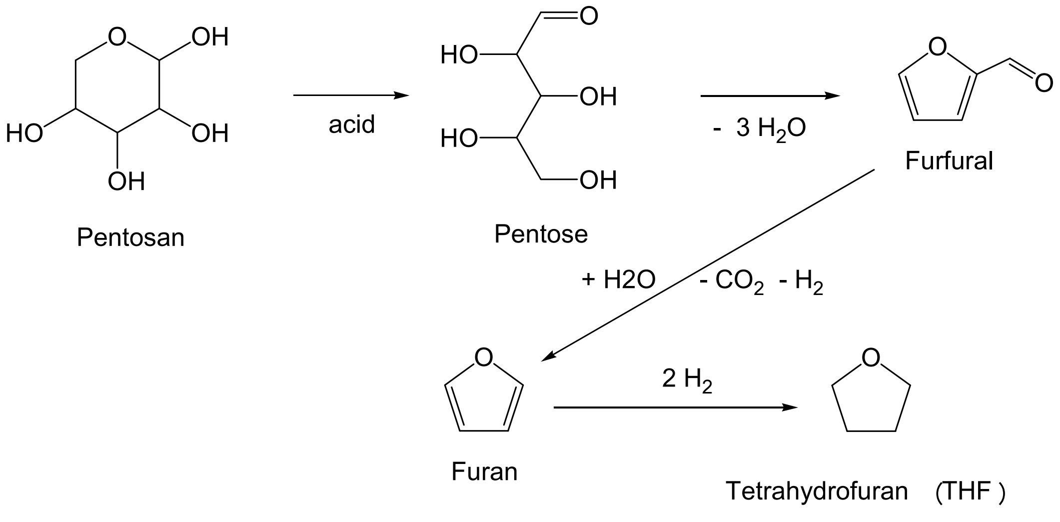

Table A-IIS.1. Approximate THF Prices

Crude Oil, \$/bbl	THF Price, ¢/lb
30	75
50	110
70	140

Your design must consider the disposition of the waste streams, including the carbon dioxide/hydrogen produced, as well as the aqueous liquid and solid wastes.

Some additional data:

Corn productivity is 150 bushels/acre.
10% of the land in this region grows corn.
Dry corn cobs contain about 30% pentosan.
The yield of pentosan to furfural is typically 50%.

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A-IIS.12.8 Diethyl Succinate Manufacture Within A Biorefinery [PROC]
(John Wismer, Arkema, Inc., January 2008)

Biorefineries convert biomass into a variety of useful chemicals. At present, the overwhelming majority of processed biomass, mostly corn starch, is converted into ethanol. Generous government subsidies have spurred significant capital investment to the extent that overcapacity has become a concern. One way to address this potential overcapacity is to retrofit such an ethanol plant into a biorefinery capable of making other high-value products.

The U.S. DOE has been promoting succinic acid ($C_4H_6O_4$) as one such product. In fact, it has recently licensed a succinic acid process to a partnership that plans to build a demonstration plant[1]. A drawback to this concept is that succinic acid is a solid. The cost of solids-handling both on the producer and consumer end is a disincentive to developing high-volume applications. A solution to this problem would appear to be the on-site esterification of succinic acid to diethyl succinate (DES or $C_8H_{14}O_4$). Fortunately, DES appears to have a high-value as a diesel fuel additive[3], where it can be used to prevent carbon build-ups. Other chemicals, most notably dimethyl ether (DME), can be used for this purpose, and consequently, the selling price of DME can be used as a benchmark for the value of DES. A discount may be required relative to DME to account for the apparent lower heat of combustion of DES.

The infrastructure of a corn starch-based ethanol plant makes it especially amenable to DES production. It hydrolyzes the starch to an aqueous glucose solution, which can be used as a feedstock for succinic acid fermentation. To make succinic acid, the fermentation reactor uses a genetically engineered strain of E.coli bacteria that steers the metabolic pathway to succinic acid[2,6]. This reaction path uses both aerobic and anaerobic steps. Carbon dioxide is consumed in the anaerobic step. Rather than produce succinic acid, succinate salt is produced to allow for pH control in the reactor. Acetic acid is the major non-selective by-product.

Following fermentation, the cell culture must be removed by any one of a number of methods, such as low shear centrifugation[12], ultrafiltration[13], or dialysis[4]. This is followed by a step that regenerates the acid either chemically or by electrodialysis[4]. Then, succinic acid can be recovered by evaporative crystallization. When inorganic salts are formed in the acid regeneration step, the crystallization must be designed to precipitate succinic acid while keeping the inorganic salts in solution[9,10,11]. However, rather than drying the succinate acid crystals, the wet crystals can be digested directly into ethanol, with conditions specified to ensure complete miscibility[8,9].

The esterification reaction occurs easily in the liquid phase with the aid of a catalyst[5]. Several reactor configurations are possible. In one concept, a CSTR is coupled with a pervaporation membrane to remove water as it is formed and relieve any reaction equilibrium barriers. The water-free organic effluent containing DES, ethanol, and residual succinic acid can be distilled in a series of columns that appear devoid of azeotropes[5].

The major advantages of converting an ethanol plant to a DES-capable biorefinery are:

- Relative to ethanol, DES manufacture preserves more of the energy inherent in the glucose molecule. Much of the criticism of the ethanol technology centers on its poor energy balance.

This is partly because much of the energy in the carbon-carbon bonds of the glucose molecule is wasted in the fermentation. Part of your design study should include a life-cycle analysis of energy consumption.

- The DES process is a consumer of carbon dioxide whereas the ethanol process is a producer. At the current state of government policy, this is more of a public relations advantage than an economic one. Nonetheless, it helps address the complaint that ethanol dumps much of the biomass-based carbon into the atmosphere before converting the remainder to useful energy.

- The DES process uses a large quantity of ethanol, which is readily available from the ethanol plant. Furthermore, this ethanol does need not be anhydrous. The process can probably use ethanol at its azeotropic composition with water (95 wt%). The ethanol can be transferred internally at production cost.

Your client is the owner of world-scale ethanol plants in the Midwest. He wants to know the cost and feasibility of retrofitting one of these plants to make DES as a co-product. He can already supply the glucose containing hydrolysate from existing capacity. His ethanol plant has a capacity of 200M gals/yr. He would like the DES capacity to be 400M lbs/yr.

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A-IIS.12.9 1,3-Propanediol from Corn Syrup [PROC]
(Bruce Vrana, DuPont, January 2008)

1,3-Propanediol (PDO) is used as a monomer, along with terephthalic acid, in polytrimethylene terephthalate (PTT). PTT, used in fiber and resins, has physical properties similar to nylon and chemical properties similar to polyethylene terephthalate. PDO also has many other applications in resin, fiber, and specialty chemicals markets.

Shell and DuPont have produced PDO via a chemical route for a few years. In 2006, however, DuPont commercialized the first large scale industrial fermentation to make a bulk chemical – PDO – in a joint venture called DuPont Tate & Lyle Bioproducts in Loudon, TN. The fermentation process uses 40% less energy than the chemical route, produces fiber grade product of higher purity than the chemical route, and uses a renewable resource as feedstock.

95DE corn syrup is the feedstock for the organism, a genetically modified E. coli. The 95DE (dextrose equivalents 95wt%) is a commodity that can be purchased for $0.10/lb from a corn wet mill. Table A-IIS.2 gives a typical composition of 95DE.

Table A-IIS.2. Typical carbohydrate profile of 95DE (% by weight, dry basis)

Dextrose	95.0
Maltose	3.0
Maltotriose	0.5
Higher saccharides	1.5

In addition to the 95DE, the organism requires a variety of nutrients, mostly inorganic salts; details will be provided later. The fermentation is aerobic, with a maximum oxygen uptake rate of 100 mmol/liter/hr. Ammonia is the preferred nitrogen source for the organism. The overall fermentation reaction may be written as:

$$37\ \text{Glucose} + 3\ NH_3 + 10\ O_2 \rightarrow 50\ \text{PDO} + 3\ \text{Biomass} + 60\ CO_2 + 16\ H_2O$$

Experimental fermentation data which will be the basis for your design will be provided later. Respiration of the E. coli liberates 460 kJ/mol of O_2 consumed.

Sterility in the fermentation area is a significant concern. Suitable measures must be taken to ensure that no adventitious organisms enter the process, eating feedstock and generating undesired products. Everything entering the fermenter must be sterile, except, of course, the innoculum.

The organism is a genetically engineered non-pathogenic strain of E. coli. Physical containment and control technology must at a minimum comply with Toxic Substances Control Act (TSCA) Part 725.422. Facilities must be designed to physically contain the live organism. It is unlikely that the highly engineered organism could survive in the wild. Nonetheless, prior to removal from containment, the organism must be deactivated or killed and then properly disposed of. Landfill is adequate for final disposal. Likewise, operating vents and spills that could contain live organism are to be contained and treated. The operating vent could be treated with a scrubber using a low concentration of bleach. Spills could be sent to a tank and heated to sterilization temperature prior to discharge.

Between fermentation batches, the fermenter is cleaned and sterilized to begin another batch. Your design may include multiple fermenters. You also need to provide facilities to grow the organism beginning each batch with a 1 mL vial in the lab containing 10 mg of live organism.

After fermentation, the biomass may be filtered from the broth, but a filter aid is needed to make the filter cake easier to handle. It is your decision as to whether the cells should be disrupted. If the cells are not disrupted, a 1wt% PDO yield loss may be assumed to occur due to PDO inside the cells. However, the whole cells would also contain about 90% of the salts added as nutrients.

The filtered broth may be ion exchanged to remove the remaining salts, using a mixed-bed system. The broth may also be concentrated in an evaporator at any point in the process, reducing the equipment size but increasing the energy consumption. If you concentrate beyond about a 5:1 ratio, you should consider boiling point elevation both by the PDO and the salts, as well as salt solubility limits. Reverse osmosis could also be considered for removal of the salts.

The refining process must purify the product to its final specification as shown in Table A-IIS.3. Distillation is considered a reasonable approach, as long as temperatures are held below 170ºC.

Table A-IIS.3. PDO Specifications

Specification	Value
Purity on dry basis, wt%	99.98
Glycerol, ppm	50
Mono-functional alcohols, ppm	500
Water, ppm	500
Metals, ppm	0.5
Appearance	Clear

Your company has assembled your team to develop a plant design and economic estimate for a 100MM lb/yr PDO plant. Your marketing organization can sell (or transfer to other company operations) PDO for $1/lb. All prices referenced here are in 2008 dollars. You may use any other U.S. DuPont patents, such as U. S. Patent 7,211,699, as well as any literature published by DuPont authors.

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.

Reference
U. S. Patent 7,135,309 to DuPont

A-IIS.12.10 Biobutanol as Fuel [PROC]

(Gary Sawyer, Lyondell Corp., January 2008)

Just as sugars can be fermented into ethanol, there are strains of bacteria that convert sugars to other useful chemicals. In a process widely practiced before World War II, a strain of *clostridium* bacteria produced acetone, butanol, and ethanol (the ABE process). With recent advances in genetic engineering and immobilized continuous bioreactors, the ABE process may have renewed interest for producing butanol as a biofuel [1]. Your consulting firm has been selected by the European Commission to develop the economics of a biobutanol process as part of the EU Biofuels directive [2]. The report will include a critique of biobutanol versus established ethanol economics.

Process Information

This same sugar solution used for ethanol fermentation is also potential feedstock for butanol. In two separate steps, the sugars are converted to acids, then to alcohols, with butanol being the major product [3]. Yields and product concentrations are provided in reference 3. You will need to design a recovery system for butanol. Butanol forms a heterogeneous azeotrope with water, and must have less than 100 ppm water in the final product. Ethanol can be used as a biofuel, but acetone is valued only as boiler feed fuel ($7.50/MMBTU). Interpret the data provided and justify your operating conditions considering product yields and capital costs.

Economic Information

Unlike the U.S., where fuels are priced per unit of volume, the EU directive will compare biofuels based on energy content.

Either biofuel will have its own price based on its blended value into gasoline. That is, given the price of regular unleaded gasoline, each biofuel will be adjusted for its impact on Motor Octane Number (MON), Ried Vapor Pressure (RVP), and energy content. You may use the following values for comparing fuels:

	MON	RVP, psi	BTU/gal	lb/gal
Ethanol	96	19	75,650	6.56
Butanol	78	6	95,860	6.72
Regular Gasoline	82	9	115,000	6.2
Premium Gasoline	88	9	115,000	6.2

For every 1 psi increase in RVP, the fuel is worth 1.5 ¢/gal less because gasoline producers cannot blend into their gasoline other less expensive feedstocks with high RVP. For every 1 point increase in MON, the fuel is worth 1.5 ¢/gal more, based on expected demand for premium gasoline.

Ethanol Economics: Starting from the sugar solution feeding ethanol fermentation, ethanol processing costs are 36 ¢/gal and capital for the fermentation and alcohol recovery are $1.30/gal annual capacity [4] ($52 million for 40 million gal/yr ethanol). The value of the sugar solution depends on the feedstocks, but may range from 5 ¢/lb to 20 ¢/lb contained sugars. It takes 15 lb of sugars to make one gallon of ethanol [3].

Comparative Economics: Your report should include the butanol prices needed to return 8%, 12%, and 15% ATROR on the capital investment, representing a range of investment risks. The price should be expressed in terms of dollars per unit of fuel energy, and include credits for RVP and debits for MON relative to regular gasoline. Include a sensitivity to fermentation sugar solution values. Also, compare to ethanol prices needed to get the same 8%-15% return on capital, again adjusted for fuel properties. Comment on what subsidies might be needed to incent either biofuel to enter the marketplace.

Miscellaneous data

A typical biofuels plant will produce 40-50 MMgal/yr. For utililities needed in separations, use $10 / 1000 lb of steam and 7 ¢/kWhr of electricity. For wastewater containing less than 0.5% organics, biotreatment costs are $15 / per gallons. Bio-solids are neutral value.

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A-IIS.12.11 Green Diesel Fuel: A Biofuel Process [PROC]

(Leonard A. Fabiano, University of Pennsylvania, January 2008)

In keeping with the environmentally-conscious design of chemical processes, UOP and Eni S.p.A. propose the UOP/Eni Ecofining^{TM} process to produce diesel fuel from vegetable oil. This novel process utilizes catalytic saturation, hydrodeoxygenation, decarboxylation, and hydroisomerization reactions to produce an isoparaffin-rich diesel fuel from a renewable feedstock containing triglycerides and fatty acids.

The resultant biofuel product has a high cetane value, a lower gravity, good cold flow properties, and excellent storage stability. Green diesel is completely compatible for blending with the standard mix of petroleum-derived diesel fuels, thus providing significant value to the refiner.

The primary feedstock for this technology is vegetable oil, such as soybean, palm, jatropha, and rapeseed oils. A typical plant oil contains 10-12 wt% oxygen, a complication that must be handled properly. These oils consist primarily of triglycerides with 1-2 wt% fatty acid. Other lower cost materials such as tall oil, tallow oil, fish oils, and waste greases can be used as feedstock. In some cases, pretreatment may be necessary to remove contaminants such as solids or salts.

The simplified process flow diagram in Figure A-IIS.18 shows the feedstock routed to the catalytic reactor where it is combined with hydrogen, brought to reaction temperature, and then converted by the series of reactions noted above to produce a branched-paraffin-rich diesel fuel.

The water and CO_2 formed by the deoxygenation reactions are separated from the deoxygenated hydrocarbon product. The resultant liquid is fractionated to remove the small amount of light fuel byproduct. Excess hydrogen provided to the reactor is recovered and recycled to maintain the required hydrogen partial pressure. Hydrogen is added to balance both the chemical consumption and solution losses.

Your team is to design a process to handle 6,500 barrel/day of vegetable oil to produce a green biodiesel with superior properties for refiners to use in upgrading their diesel pools. You should determine the government subsidy, if necessary, required to achieve a return on investment of at least 15% after taxes.

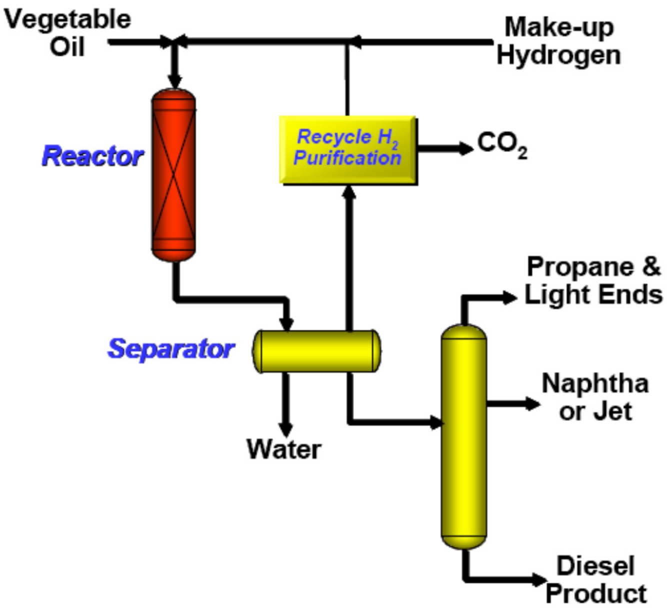

Figure A-IIS.30. Simplified process flow diagram

You will have to search for a suitable location for the facility given the feedstock availability and product end use. References are included to assist in assigning approximate feedstock costs. While data may be available providing estimates of government subsidies required by others, your team will work to achieve a design that requires smaller subsidies.

References

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A-IIS.12.12 Algae to Alkanes [PROC]
(John Wismer, Arkema, 2010)

Of all the embryonic biofuel technologies, the ones involving cultivating, harvesting, and processing hydrocarbons from algae are drawing the most research attention. The NREL lists over thirty companies targeting this area. Some (such as OriginOil) are publicly traded. Most are still in the venture capital stage. In addition, some of the major oil companies (Shell, Chevron, Exxon) have already announced strategic partnerships. The advantages of algae are numerous: 1) its cultivation does not encroach on the food sector, 2) its biomass productivity per acre far exceeds that of any agricultural commodity, 3) it produces lipids that can be converted easily to biodiesel or fuel range hydrocarbons.

The conversion of algae to useful biofuels can be thought of as occurring in three process modules: 1) algae cultivation, 2) lipid extraction, and 3) lipid conversion. For all three modules, there are a variety of different approaches with widely varying claims as to cost effectiveness. Your client is a venture capital firm that invests in alternative energy and has hired Penn Consultants to evaluate the long term potential for biofuels from algae. Your client has been burned in the past by biofuel ventures and is well aware of the problems of negative energy balances, and water and land use issues that have bedeviled this industry. NASA has expressed skepticism that terrestrially cultivated algae could become cost competitive due the high energy requirements of processing[12]. Your client wants to know if, under a reasonable best case scenario, a large-scale algae-to-fuel venture would be profitable. In this sense, you are free to pick and choose the best available technology for the three steps of the supply chain.

There are three competing approaches to the first module. The first involves cultivation in open-air “raceway” ponds, but they have been hampered by contamination and low growth rates. Another is a compact photo-bioreactor with complex internals designed to optimize the growth environment. The third is a hybrid approach – one that utilizes agricultural resources and infrastructure, yet cultivates the algae in enclosed tubes. The reactor design is potentially quite complex. It requires accounting for carbon dioxide concentration, light exposure, and mass transfer from gas to liquid. Furthermore, nitrogen starvation is sometimes intentionally used to maximize lipid production at the expense of the protein fraction. Rather than tackle the details of this design, you can use References 1-3 to develop a basic material and energy balance and assume the productivities are as given. Site selection will be important since a carbon dioxide source, water access, and adequate sunlight are all design considerations.

For the second module, the key is extracting the desirable triglyceride fraction way from the proteins, carbohydrates, phospholipids, and nucleic acids that make up the rest of the biomass. As a chemical extraction agent, hexane seems to be the solvent of choice. Alternatively, OriginOil claims that algae cell lysis and lipid removal can be induced by combinations of pH modification, microwaves, and ultrasonic pulses[4,5]. Their technology apparently disrupts the cell wall enough to allow most of the lipids to escape. Their patent application has not been published yet. However, the process is illustrated on their website and appears to show a lipid fraction rising to the surface of an aqueous layer while the protein laden residue sinks to the bottom[6]. OriginOil is claiming dramatic reductions in the cost of lipid extraction. You can use a “black box” approach on the process – a material balance based on a lipid-rich algae strain.

The conversion of the lipid fraction to useful products has a number of options. One approach is to convert it to biodiesel[8]. The disadvantage of this is its low energy content and high viscosity relative to straight hydrocarbon diesel. Another approach chemically processes the lipids to alkanes that could be used in fuels ranging from gasoline to jet fuels[7]. These are relatively high-value products with broad acceptance in a variety of markets. Your client is particularly interested in the potential for this technology. This process module involves conventional chemical processing and should be done in sufficient detail to allow for an evaluation of lipids processing economics irrespective of the cost of the feedstock.

References

Algae Cultivation

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Lipid Isolation

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A-IIS.12.13 Algae to Biodiesel [PROC]
(Warren D. Seider, Univ. of Pennsylvania; Kimberly Ogden, Univ. of Arizona, 2011)

During the Spring 2010, a design project [1] focused on the growth of algae using the SIMGAE cultivation process [2-4], (2) OriginOil's process for lipid extraction [9-11], and (3) a process to convert the lipids to alkanes (green diesel) [15-16]. A profitable overall process was designed, although the investment costs were very high. Since then, a research project to convert algae to biofuels by the National Alliance for Advanced Biofuels and Bioproducts (NAABB) was funded by DOE ($49 million). The Univ. Arizona and Penn are collaborating on a portion of this project. Furthermore, some of the major oil companies (e.g., ExxonMobil) have announced significant development efforts. The advantages of algae are numerous: (1) its cultivation does not encroach on the food sector, (2) its biomass productivity per acre far exceeds that of any agricultural commodity, (3) it produces lipids that can be converted easily to biodiesel or fuel-range hydrocarbons.

In this design project, the focus will be on exploring the processing technologies described below, and likely other promising technologies that are proposed in the next few months.

Algae Cultivation

Recently, the *heteroboost* photosynthesis-fermentation process was proposed to generate lipids for biodiesel production [5]. First, *chlorella protothecoides* algae are grown autotrophically to fix CO_2. Then these are metabolized heterotrophically using glucose to significantly increase the lipid yield.

Yet, another cultivation process was recently proposed by Teymour and coauthors [6] involving a farm of artificial algae trees whose trunk and branches are filled with algae solution and exposed to solar energy.

More recently, a kinetic model has been proposed to estimate the rate of algae growth as a function of the light intensity and the concentration of nitrogen nutrients [7]. This model can be used to better estimate the size and cost of various conversion processes, including photobioreactors. Also, data taken in "raceways" at the Univ. of Arizona are showing the impact of temperature on the algae growth rate [8].

Based upon the data in [5-8], better estimates of the installation and operating costs of cultivation processes, as compared with SIMGAE process costs, should be obtained. It is anticipated that lower-cost processes will be designed.

Lipid Extraction

The OriginOil process involves the generation of sonic waves and microbubbles at high frequency [9-11]. Energy costs are claimed to be 10% of conventional processing costs. An objective of this design project will be to gain better estimates of these costs – although this aspect of the design is likely to be deemphasized.

Lipid to Biodiesel

The conversion of the lipid fraction to useful products has several options [12-14]. One approach is to convert it to biodiesel [15-16]. Recently, two papers discuss the ASPEN PLUS simulation of a potential process to produce biodiesel [17-18]. Your group will seek to improve upon these designs and will attempt to carry out design optimization. This will include sizing and costing the trans-esterification reactor and the remainder of the processing equipment.

Life-Cycle Analysis

When estimating the profitability of your entire process to convert algae to biodiesel, your group will carry out a life-cycle analysis (LCA) [19]. To achieve a sustainable design, it is important that no net CO_2 be produced, that waste water be recycled, and the like. You will attempt to optimize the profitability of your design, as well as its sustainability.

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A-IIS.12.14 Glycerol to Ethanol [PROC]

(Bruce M. Vrana, DuPont, 2009)

Glycerol is a byproduct of biodiesel manufacture, with relatively few industrial uses. As the production of biodiesel increases, particularly in Europe due to government regulations but also in the U.S. due to public demand for renewable fuels, the price of glycerol is expected to continue to decrease.

Your research organization has recently isolated a naturally occurring *E. coli*, code-named Penn09, that will ferment glycerol to ethanol and a small amount of succinic acid. Ethanol is in high demand for transportation fuel, and succinic acid is a high-value specialty chemical.

You have been asked to determine whether this technology could be commercially successful, using the following assumptions, determined by your research director. You need to design a plant that will make 50MM gallons per year of fuel ethanol using this technology and estimate the economics.

Crude glycerol is a good substrate for this strain of *E. coli*. The salts in the glycerol contain all the nutrients that the organism needs to survive and reproduce. The fermentation is anaerobic, and the overall reactions can be written as:

$$\underset{\text{Glycerol}}{CH_2OH\text{-}CHOH\text{-}CH_2OH} \rightarrow \underset{\text{Ethanol}}{CH_3\text{-}CH_2OH} + CO_2 + H_2 \qquad (1)$$

$$\underset{\text{Glycerol}}{CH_2OH\text{-}CHOH\text{-}CH_2OH} + CO_2 \rightarrow \underset{\text{Succinic acid}}{HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH} + H_20 \qquad (2)$$

Assume that 98% of the glycerol is converted in reaction 1, 1% of the glycerol is converted in reaction 2, and 1% is converted to biomass. The overall reaction rate is 1.6 g EtOH formed/L of reaction volume/hour. Feed only enough glycerol to the batch fermenter to reach a final ethanol titer of 100 g/L.

Sterility in the fermentation area is a significant concern. Suitable measures must be taken to ensure that no adventitious organisms enter the process, eating feedstock and generating undesired products. Everything entering the fermenter must be sterile, except of course for the innoculum.

The organism is a naturally occurring strain that poses no known hazards to humans and thus is less stringently regulated than if it were genetically modified. Nonetheless, it would be prudent to design facilities to physically contain the live organism. Prior to removal from containment, the organism must be deactivated or killed and disposed of properly. Landfill is adequate for final disposal. Operating vents and spills that could contain the live organism are to be contained and treated. The operating vent could be treated with a scrubber using a low concentration of bleach. Spills could be sent to a tank and heated to sterilization temp. prior to discharge.

Also fed to the fermenters is your *E. coli* inoculum, which you produce in a separate seed fermentation train. The biochemistry of the organism is outside the scope of this project. Fortunately, your research organization has developed a simple scenario for your use. The organism will come from 1 ml vials stored in a freezer on site. It will be grown in successive stages each 20 times the size of the prior stage, each stage taking 24 hours. After 24 hours, it is put in the next larger vessel along with water and a sugar source. If you use less than a 20 X factor for any stage of fermentation, you must still allow 24 hours for that stage of fermentation to take place. 10 liters is the largest stage that can be grown in the lab before transferring to the first seed fermenter in the plant. Lab scale fermentations will use clean glycerol and other nutrients, the cost of which can be ignored for this evaluation, along with the cost of the initial vial of organism. (Note, however, that the vials do have a cost, so you may only use one vial per production fermenter batch.) Once the laboratory-produced seed is taken to the plant seed fermentation train, each stage of seed fermentation will be fed with plant water and enough glycerol to produce the maximum titer of 100 g/L ethanol before transfer to the next larger seed fermenter, or ultimately the production fermenter(s). Your material and energy balance should include the amount of water and glycerol fed to the plant seed train.

Fermentation is the only batch step in the process. Your design must consider how to best match up fermentation with the continuous back end of the plant. A Gantt chart may be helpful to illustrate the filling, fermentation, emptying and cleaning process for however many production and seed fermenters your design employs.

Fermentation off-gas will, unlike in ethanol plants, contain a significant amount of hydrogen, as shown in the stoichiometry above. Your design needs to handle this stream in a safe, environmentally acceptable and economical manner before discharge to the atmosphere. You may assume a slight positive pressure in the fermenters, say 5 inches of water gauge, which will help keep the fermentation anaerobic.

Downstream of fermentation, it is expected that this process will have many similarities to the fuel ethanol process used in the U.S. and Brazil. Should you wish to use the fuel ethanol industry process standard for drying ethanol from near the azeotrope to 99.5% purity, molecular sieves, you need to know that regeneration of the molecular sieves requires recycling 20% of the dry ethanol product back to the sieves. This regeneration stream, which on average contains 37% water after leaving the molecular sieves, must then be recycled back to your separation process. The composition of the regeneration stream varies with time, so your design should take that into consideration. A brief, but informative, discussion of the ethanol molecular sieve process is contained in Aden et al. (2002).

A packaged unit for drying ethanol with molecular sieves costs $2.5 million to process 34,000 lb/hr on a pure ethanol basis. The feed is saturated vapor at 1 atm, 92% ethanol, 8% water by weight. The products are saturated liquid at 1 atm. Scale the cost with a 0.6 exponent. Electrical usage is 0.002 kWhr/lb of product. Steam usage is 0.04 lb/lb of product for additional heating. Cooling water usage is 3 gal/lb of product. Since this is a packaged unit, it includes piping, instrumentation, etc., and thus should have different installation factors than most other purchased equipment.

Ethanol must be denatured on site with 2-5% by volume of unleaded gasoline, to conform to the Bureau of Alcohol, Tobacco and Firearms regulations (preventing human consumption of untaxed alcohol). Prior to denaturing, it must be 99.5% pure ethanol.

Corrosion and cleanliness dictate that most process equipment be fabricated from 304 stainless steel. This holds for any equipment that contains water. Exceptions include corn silos, product storage tanks, and any distillation or other separation systems that contain less than 1% water, which may use carbon steel.

Since your product is intended for transportation fuel use, it is imperative that the process be as energy efficient as possible. The current benchmark for energy use in a fuel ethanol plant is about 35,000 BTU/gallon of product. (This is calculated as the amount of heat and electricity needed by the process, not the amount of fuel consumed in the boiler.) You should certainly be able to surpass that benchmark, due to differences in the process.

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.

Your purchasing organization believes that the equilibrium price for byproduct glycerol is $0.15/lb, delivered to your U. S. Gulf Coast plant. Your marketing organization believes they can sell denatured ethanol for $2.50/gal. Succinic acid can be sold for $2.00/lb provided it meets normal purity specs. Unleaded regular gasoline used for denaturing costs $2.50/gallon wholesale. All prices referenced here are in 2009 dollars. Obviously, you will want to test the sensitivity of your economics to these price forecasts.

Undoubtedly, you will need additional data beyond that given here. Cite any literature data used. If need be, make reasonable assumptions, state them, and whether your design or economics are sensitive to the assumptions you have made.

References

The Renewable Fuels Association web site has a good description of the fuel ethanol process and industry. http://www.ethanolrfa.org

A good model for much of the dry grind ethanol process is discussed on http://www.intelligen.com/literature.shtml which links to a paper by Kwiatkowski et al. This includes a SUPERPRO DESIGNER model that works with their evaluation version of the software. Note, however, that SUPERPRO DESIGNER does not handle VLE rigorously and thus is not suitable for designing this process.

Dharmadi, Y., A. Murarka, and R. Gonzalez, “Anaerobic Fermentation of Glycerol by *Escherichia coli*: A New Platform for Metabolic Engineering”, Wiley InterScience, 5/20/2006 contains a description of the biochemistry in a similar organism.

Aden, A., et al., “Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover”, NREL/TP-510-32438 (2002).

A-IIS.12.15 Sunlight to Convert CO_2 into Transportation Fuels [PROC]

(Matthew Targett, LP Amina, Beijing, China, 2014)

Overview

Investigate the science and economics of a sunlight to fuels technology. Design the process and facility using engineering and financial projections, including best, base and worst case scenarios. Take a systems approach in producing your business model.

Background on Technology

Reversing combustion, though theoretically possible, has long been considered technologically and economically impractical, but a prototype at the Sandia National Laboratories is challenging conventional wisdom by recycling carbon dioxide into fuels. Developed by Rich Diver, the Counter Rotating Ring Receiver Reactor Recuperator (CR5) uses heat from concentrated solar power to drive highly endothermic reactions involving metal oxides, CO_2 splitting and water splitting in rotating loops. You will combine the CO and H_2 (produced directly or indirectly) from the CR5 in a Fischer-Tropsch reactor to produce transport fuels and chemicals.

The technology involves concentrated solar energy, in which mirrors focus and reflect sunlight onto the CR5 to produce temperatures higher than 2000°C. In the CR5 dish modules, the concentrated solar energy heats loops of metal oxides to reduce them to their base metals by removing oxygen. The reduced metals are rotated into a lower temperature chamber with carbon dioxide and, being highly reactive, the metals strip oxygen atoms from the gases, producing carbon monoxide and metal oxide. The loops continue rotating between the concentrated solar-heated chamber and the cooler, carbon dioxide chamber for continuous production of carbon monoxide. Water can be used in place of carbon dioxide to produce hydrogen; otherwise, part of the carbon monoxide produced by the CR5 can be used to strip oxygen from water molecules in a separate reactor that you will design. The products, carbon monoxide and hydrogen, will then be feedstocks in your Fischer-Tropsch process to produce transport fuels.

The reactions in the CR5 dish modules (reduce metal oxides to produce CO from CO_2):

$$Fe_3O_4 \rightarrow 3\ FeO + 1/2\ O_2$$
$$3\ FeO + CO_2 \rightarrow Fe_3O_4 + CO$$

$$CO_2 \rightarrow 1/2\ O_2 + CO$$

If you decide it is more practical to do so, you can design a portion of your CR5 modules to use water instead of CO_2 to gain the hydrogen needed for the Fischer-Tropsch process. If not, you can design another reactor to produce H_2 by the water-gas shift of CO from the CR5 process, e.g.:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The CO and H_2 you produce will be fed into a Fischer Tropsch process and produce a transport fuel based on your analyses. An example of a reaction is below:

$$8\ CO + 17\ H_2 \rightarrow C_8H_{18} + 8\ H_2O$$

Tips on Commercialization Portion

In your economic assessments and facility cost predictions, some aspects you may want to consider are:

- fixed and variable costs (e.g., cost of facility and labor)
- return on investment
- location of facility
- price projections of each raw material
- feedstock for the carbon dioxide
- useful by-products
- price projections of the final product (your fuel of choice)

In judging the competitiveness of each scenario, you may want to take into account the political and economic landscape of the energy industry and climate change challenge. This includes other technological developments in transport fuels that might influence spot prices, such as new pipelines or Bakken crude that influence WTI crude, which is the US benchmark. Also take into account the changing nature of energy policy, such as incentives for renewable fuels and regulations that may give you an upper hand.

Some companies working on Concentrated Solar Power include: Abengoa, Bright Source, Torresol Energy. Some facilities researching high temperature redox other than Sandia include DLR German Aerospace Center, Paul Scherrer Institute and ETH Zurich, and the Weizmann Institute in Israel.

References

Sunshine to Petro: Solar Recycling of Carbon Dioxide into Hydrocarbon Fuels. *Sandia National Laboratories.* <http://energy.sandia.gov/wp/wp-content/gallery/uploads/S2P_SAND2009-5796P.pdf>

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Sandia's Sunshine to Petrol Project Seeks Fuel from Thin Air. *Sandia National Laboratories.* 5 Dec. 2007. <https://share.sandia.gov/news/resources/releases/2007/sunshine.html>

Chen, K. Three-Dimensional Modeling of Solar Thermochemical Splitting of CO_2 in a CR5. 2011.

Mayer, LJ. Thermal Recuperation Modeling of a Solar Thermochemical Reactor. 2011.

Steinfeld A. Design Aspects of Solar Thermochemical Engineering. 1999.

T-Raissi, A. Analysis of Solar Thermochemical Water-Splitting Cycles for Hydrogen Production. 2003.

Steinfeld, A. Solar Thermochemical Production of Hydrogen—A Review. 2004.

Rennels, R. Solar Thermochemical Hydrogen Production Project – Progress Toward Industrial Scale Water Splitting. 2008.

Note: The creator of this project is not based in Philadelphia. Many or all interactions will be through SKYPE, phone and/or email.

A-IIS.13 ENVIRONMENTAL – MISCELLANEOUS

A-IIS.13.1 Combined Cycle Power Generation [PROC]

(William B. Retallick, Consultant, January 2001)

The wave of the future in power generation is the combined cycle, in which gas turbines are combined with steam turbines, with the hot exhaust from the gas turbine used to generate steam. The combined cycle is a cascade of heat engines operating over temperatures from 1200-1300°C to about 30°C. This broad temperature range renders the combined cycle efficient.

A gas turbine is comprised of three main parts. The compressor compresses the inlet air to the pressure in the combustor, with fuel injected into the latter. Hot combustion gases are expanded in the turbine, which drives the compressor, with the bulk of the power produced by the turbine consumed by the compressor.

The final stage(s) in the turbine comprise a "free" turbine. These stages are mounted on the shaft of an electric generator, rather than the shaft of the main turbine. To generate 60-cycle power, the free turbine rotates at 3,600 RPM. Note that the main turbine rotates at 8,500 RPM. The exhaust gas from the free turbine is sent to the steam generator.

There are two kinds of steam turbines. In a condensing turbine, the exhaust steam is condensed using cooling water, at a pressure determined by the temperature of the cooling water. In an extraction turbine, the exhaust steam is not condensed, rather it is exhausted at an intermediate pressure to be reheated and used in a condensing turbine.

The efficiency of the combined cycle is determined almost entirely by four parameters:

- The temperature of the combustion gas entering the turbine, here assumed to be 1,250°C.
- The efficiency of the compressor, here assumed to be 89%.
- The efficiency of the turbine, here assumed to be 90%.
- The efficiency of a steam turbine, here assumed to be 89%.

The gas turbine is operated at a compression ratio that maximizes the work produced per weight of air, as explained in the first reference. Your turbine is equivalent or similar to the W501G turbine described in the second reference. Its electrical power output is 230 MW, which fixes the size of your combined cycle. You are to configure a set of steam generators and steam turbines that provides the economic-optimum amount of electric power from the heat in the exhaust from the free turbine.

Design Basis

The fuel gas composition (mol %) is:

Methane	96
Ethane	3
Propane	1

The gas is delivered at 400 psig.
The ambient air is 25°C and 40% relative humidity.
Cooling water for the condensing turbine is at 30°C.
The efficiency of an electric generator is 98%.
The plant is located in Pennsylvania.

Your report should include:

The plant efficiency, kwh of fuel per kwh of electrical power.
A graph of the investor's rate of return (IRR) as it varies with the selling price of power, for different costs for the fuel gas.

References

Chem. Eng. Prog., May, 2000, page 69.
Diesel and Gas Turbine Worldwide, July-August, 2000, page 42.

A-IIS.13.2 Waste Heat Recovery [PROC]

(Adam A. Brostow, Air Products and Chemicals, 2010)

”Uncommon men require no common trust; give him but the scope and he will set the bounds.” – Friedrich von Schiller

Introduction

Energy efficiency is an important issue due to, among other factors, environmental regulations limiting CO_2 emissions. Most of the electrical energy supplied by the grid originates with the burning of fossil fuels.

There is an increased incentive to recover heat from relatively low-temperature sources (so-called low-grade or waste heat) and convert it to power. Low-grade heat sources may include hot compressor discharge, hot automobile exhaust, hot streams leaving a chemical reactor, hot geothermal springs, other sources of renewable energy, etc. Most of this heat is wasted because there is no economical way to convert it to power.

Background Information

Figure 1 shows a basic Rankine power cycle. The low-temperature hot stream heats the working fluid in the heat-recovery heat exchanger (HRHX). The working fluid is pumped, heated up, and typically vaporized in the HRHX, expanded in an expander (EXP) connected to a generator, and condensed in the condenser (CND).

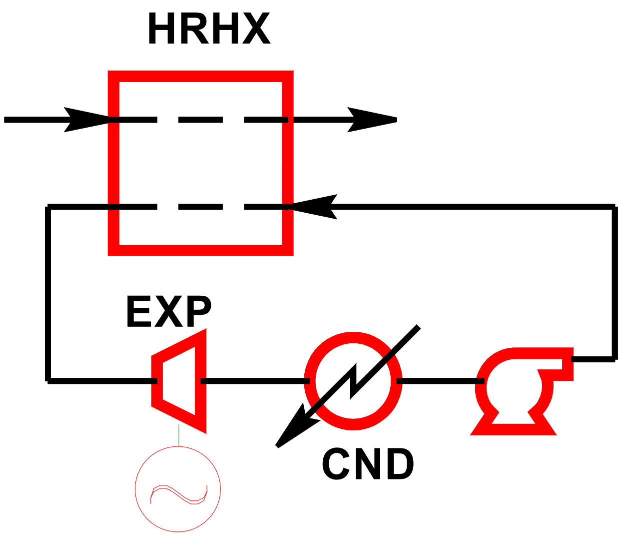

Figure A-IIS.31. Rankine cycle

The disadvantage of a conventional Rankine cycle is its relatively low efficiency due to large temperature differences between the hot and cold streams in the HRHX. The colder the heat source, the lower the efficiency.

U.S. Patent 7,278,264 describes a new cycle, a variation of the Rankine cycle that uses liquid or dense supercritical fluid (below its critical temperature, but above its critical pressure) instead of vapor in the expansion step.

Figure A-IIS.32 (Figure 3 in the patent) shows one implementation of the cycle. Stream 110 is compressed in compressor 112. The resulting hot stream 114 is cooled in the heat-recovery exchanger 116, and exits the exchanger as stream 118. Stream 114 is the source of low-grade heat.

Liquid working fluid in stream 120 is heated in heat-recovery exchanger 116 by indirect heat exchange with stream 114. The resulting stream 122, which is substantially liquid, is expanded in a two-phase dense-fluid expander, 124, to produce stream 126 containing mostly liquid with some vapor. Power generated by 124 can be used in the cycle or exported to the grid.

Stream, 126, at an intermediate pressure, is sent to phase separator 326, which produces vapor stream 327 and liquid stream 324. Vapor stream 327 is reheated in exchanger 116 and expanded in conventional vapor expander 330 to generate additional power yielding stream 332. Liquid stream 334 is expanded in dense-fluid expander 336 to generate more power yielding two-phase stream 338. Streams 332 and 338 are combined, giving stream 340, which is completely condensed in condenser 130.

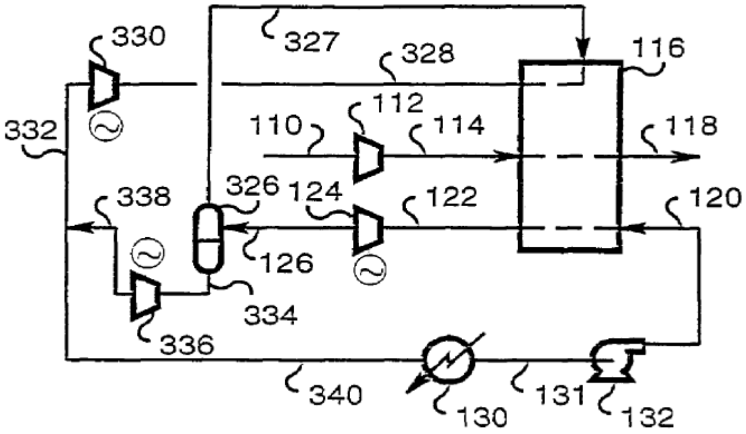

Figure A-IIS.32. Low-grade heat-recovery cycle

Other configurations are described in a patent.

Figure A-IIS.33 shows an Organic Rankine Cycle with Economizer/Regenerator (ECON) heat exchanger. Working fluid is fully vaporized in HRHX, expanded in EXP, and de-superheated in the ECON heat exchanger prior to condensation in CND and pumping. Such a cycle is commonly used in low-grade heat recovery. An example is described in U.S. Patent 7,100,380.

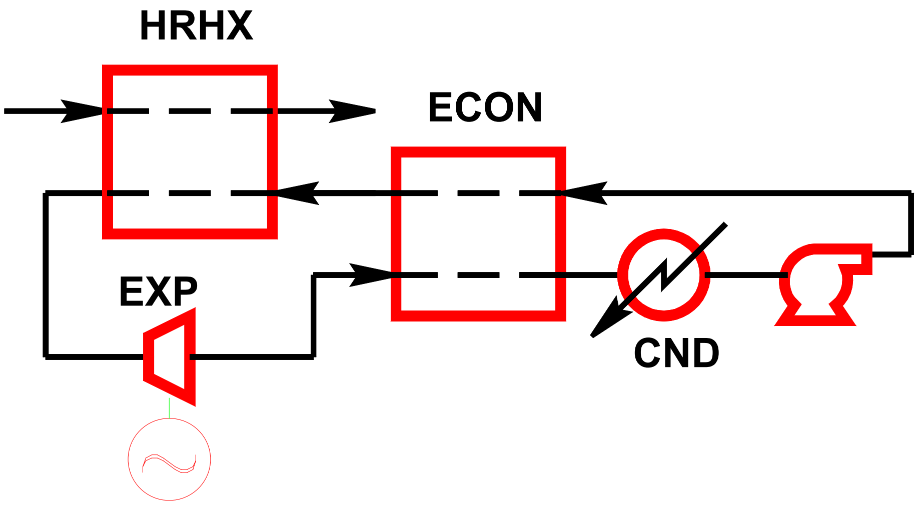

Figure A-IIS.33. Organic Rankine Cycle

Also, U.S. Patent 2007/0056284 and U.S. Patent 2008/0190135 show mixed-fluid power cycles. The use of mixed working fluids improves cycle efficiencies. Both cycles involve an additional source of high-grade heat.

Problem Statement

Air from a hot compressor is discharged at 65,000 lbmol/hr, 120 psia, and 230ºF. Typically, it is cooled to 70ºF in a shell-and-tube aftercooler. The heat is rejected to cooling water and, therefore, wasted. The aftercooler pressure drop does not exceed 5 psi.

No high-grade heat source is available.

This design project begins with an estimate of the thermodynamic availability of the hot stream; that is, the maximum work extracted when the stream is moved to its environmental state (77ºF and 1 atm).

Then, the design team will consider the alternative cycle described in U.S. Patent 7,278,264 using ammonia as the working fluid and allowing up to 30 mol% vapor from the DFE discharge and an adiabatic efficiency of 75%. Cooling water will be at 65ºF and the minimum temperature approach for the shell-and-tube condenser will be 5ºF. The heat-recovery heat exchanger is plate-and-fin with a minimum approach temperature difference, ΔT, of 2ºF and 20 NTUs, where NTU = ΔT_w / LMTD, and ΔT_w is the cooling temperature change of the warm (air) stream. For the most promising design, the design team will determine the power generated and the capital investment required. Assuming a power cost of $2,000/KW, the competitiveness of this design will be considered. Note that ASPEN PLUS can be used for simulations of the designs.

The design team will begin with the configuration in Figure 1 and, depending on progress and perceived benefit, consider other configurations such as the one shown in Figure 2 (Figure 3 of the patent).

Also, the design team will consider another way of recovering low-grade heat with the same heat source specifications as above. The team will select the cycle/method.

A possible candidate is a conventional organic Rankine cycle using pure working fluid such as propane or a mixture of components, such as hydrocarbons. Propane or another fluid will be completely vaporized in the HRHX. The amount of liquid at the expander's discharge is not to exceed 15 mole%. The expander's isentropic efficiency is 86%. Again, the power generated will be estimated – and the economics will be compared with those of the ammonia cycle. The design team is encouraged to search the literature and consider other low-grade heat-recovery methods, as well as other working fluids. The team should begin with a simple flowsheet and, if time permits, refine it to include additional features such as the economizer, etc.

Finally, if time permits, hot air at 350ºF will be considered. The design team will determine whether a break-even temperature exists – at which both cycles break even based on combined capital cost and power revenue.

In summary, the key elements of the project are to: a) determine the theoretical power limits, and b) compare novel technologies with current practice.

References

Brostow, A., *Process to Convert Low Grade Heat Source into Power using Dense Fluid Expander*, U.S. Patent 7,278,264.

Martin, C.G., and P.F. Swenson, *Method of Converting Low-Grade to Useful Mechanical Power*, U.S. Patent 3,950,949.

Johnson, R.H., *Power Recovery and Feedback System*, U.S. Patent 4,182,127.

Brasz, J.J., and J. Jonsson, *Organic Rankine Cycle Fluid*, U.S. Patent 7,100,380.

Kalina, I.K., *System and Method for Utilization of Waste Heat from Internal Combustion Engines*, U.S. Patent Application 2007/0056284 A1, March 15, 2007.

Mak, J., *Configuration and Methods for LPG Production and Power Cogeneration*, U.S. Patent Application 2008/0190135 A1, April 14, 2008.

Patent searches can be performed using http://patft.uspto.gov/netahtml/PTO/search-adv.htm

Patents can be viewed in http://www.patentgenius.com/

General description of the Organic Rankine Cycle:
http://en.wikipedia.org/wiki/Organic_Rankine_Cycle

Organic Rankine Cycle used by WOW Energies is described in:
http://www.wowenergies.com/wowgen.html.

Stinger, D., "Getting More Power from Waste Heat," *Turbomachinery Int'l.*, July/August 2004. www.turbomachinerymag.com.

A-IIS.13.3 Gas Turbine Heat Recovery [PROC]

(Adam Brostow, Air Products and Chemicals, 2012)

Background

With nuclear power investments recently reduced due to safety concerns and the discovery of shale gas in Pennsylvania, Poland, and elsewhere, natural gas, the cleanest-burning fossil fuel, is becoming more economically viable. It is usually transported across the ocean as LNG (liquid natural gas).

Figure A-IIS.34 shows an LNG plant. Natural gas (NG) is liquefied by using MR (mixed refrigerant). MR is compressed in refrigerant compressor (RCMP), cooled and liquefied in the main cryogenic heat exchanger (MCHE, typically a wound coil type), throttled though the Joule-Thompson valve (JT) and vaporized in the MCHE to provide refrigeration for liquefaction. The cycle is similar to the food refrigerator (vapor compression cycle) except that the MR boils over a range of temperatures for high thermodynamic efficiency. LNG is throttled at the cold end of the MCHE to provide low-pressure LNG product. End flash (EF) vapor is re-warmed, compressed in the fuel compressor (FC) and used as fuel in the gas turbine (GT). The GT directly drives the RCMP.

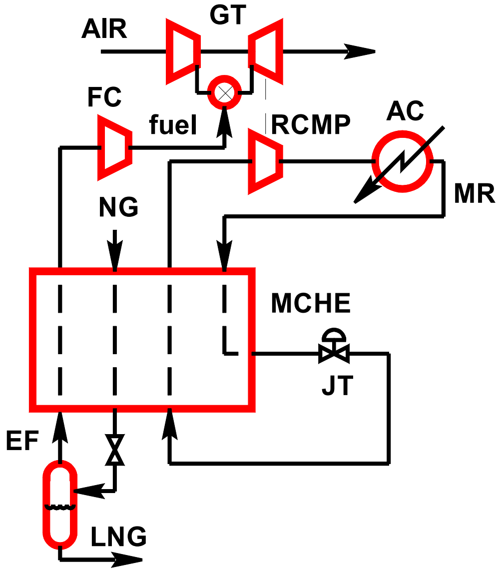

Figure A-IIS.34

Figure A-IIS.35 shows the simple gas turbine (reverse-Brayton) cycle. Air is compressed in axial compressor CMP and fed to the combustion chamber where it is mixed with fuel. The resulting mixture is burned and expanded in expander EXP to generate power or to directly drive a piece of machinery (like on Figure 1). The turbine exhaust is still very hot.

Most LNG plants are in remote locations, not connected to the grid. Some are installed on floating platforms or ships where the footprint is important. Typically, there is no economic incentive, or physical space, to recover the exhaust heat. This translates to higher CO_2 emissions and larger carbon footprints of such plants.

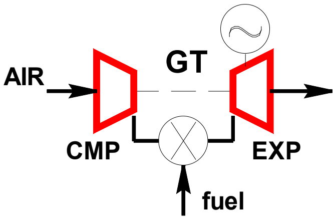

Figure A-IIS.35

Figure A-IIS.36 shows the conventional combined cycle with heat-recovery steam generator (HRSG) and a steam turbine (ST). Hot gas-turbine exhaust drives the steam cycle. Water is pumped, vaporized in HRSG, expended in the ST, and condensed against cooling water or air in condenser (CND). The cycle is not commonly used in LNG as the additional equipment cost (HRSG, ST, thermal well, steam condenser, ejectors) is prohibitive. If water is scarce, the steam condenser uses ambient air as cooling utility. Such condensers have huge footprints.

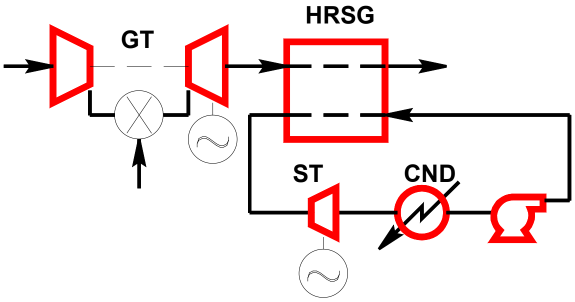

Figure A-IIS.36

There are other gas turbine cycles that can achieve the partial benefit of the combined cycle. They include, but are not limited to, direct steam injection with the waste-heat boiler ("poor man's combined cycle"), cycles using recuperator heat exchangers, and chilling of the GT's inlet.

Recent advances in reverse osmosis and other desalination techniques will make cycles involving the use of water more viable for land-based LNG plants located on the coast, and for floating plants.

All of these cycles increase power output. This allows either: (a) higher LNG production for fixed turbine sizes, or (b) the use of smaller turbines for fixed LNG production. The benefit of reduced CO_2 emissions is harder to quantify.

There is another way to recover GT exhaust heat. Instead of making the GT cycle more efficient, the exhaust heat can be used to generate refrigeration to cool the liquefaction cycle compressors ("ice from fire"). Such heat recovery includes, but is not limited to absorption refrigeration and TASHE-OPTR (thermo-acoustic, Stirling heat-engine, orifice pulse-tube refrigerator).

Since LNG production is almost directly proportional to power used, increasing the efficiency increases production. Conversely, for fixed production, higher efficiency decreases equipment size and CO_2 emissions.

Problem Statement

The LNG plant produces about 1 MTPA (million metric tons per annum) of LNG. It uses 40 MW of power. It is driven by a simple-cycle gas turbine. The gas-turbine conditions are as follows.

The compressor inlet temperature is 68°F, pressure at 14.7 psia, isentropic efficiency at 86%, and discharge pressure at 350 psia. The combustion takes place at 1,940°F. Assume the fuel is pure methane, and 5% excess air is used over the stoichiometric amount. The expander isentropic efficiency is 90% and the discharge pressure is 20 psia.

A combined cycle would use cooling water at 58°F, a 10°F temperature approach on the condenser, and a 3.6°F minimum temperature approach on the HRSG. Water to generate steam would be pumped to about 520 psia. The ST discharge pressure would be 6 psia (vacuum), with the pump efficiency at 85%.

The challenge is to improve the efficiency of the cycle, and thus, reduce the CO_2 emissions by employing the combined cycle (Figure A-IIS.36), henceforth used as a benchmark for efficiency, capital cost, and footprint, and at least two of the other simplified cycles (including those not listed here) for comparisons of cost and efficiency. The idea is to select a cycle that gives the most benefit for the least cost. For example, can one get 50% of the combined cycle's benefit for 30% of the cost?

One can assume the direct drive as the LNG liquefaction process is driven by multiple stages of compression. For example, one of the stages could be driven directly by the steam turbine.

The student design group is expected to model the gas turbine, including the combustion process, the combined cycle, and the simplified cycles, determine the efficiency, and size/cost the equip.

The LNG process also uses cooling water at 58°F. The compression power is almost directly proportional to the cooling-water temperature. The cooling duty is 140 MW. Can one use the heat recovered from the GT to generate refrigeration to chill water that can be used to either chill the GT inlet or the refrigerant compressor? Is it better to use this heat to improve the GT cycle or to use GT exhaust heat to chill the liquefaction process?

References

U. S. Patent 6,523,348
U. S. Patent 7,637,093
French Patent 2,944,095
GTPowerCycles.pdf

Much information is available online. The student group is encouraged to seek additional information and to modify/improve the process.

A-IIS.13.4 Compressed Air Energy Storage [PROC]

(Adam A. Brostow, Air Products and Chemicals, 2014)

<u>Background</u>

With the development of intermittent renewable energy sources such as solar and wind it is becoming increasingly important to economically and efficiently store excess energy to provide uninterrupted power supply. Energy storage is also important for time-of-day energy management and peak shaving.

Figure A-IIS.37 shows the general concept of CAES: compressed air energy storage. Air is compressed in a compressor CMP (that can be driven by electric motor EM) and stored in a tank. It can then be expanded in expander EXP to generate energy. Compression may be isothermal or adiabatic. Expansion may be with or without the reheat. Compressor and expander may be the same unit or different units.

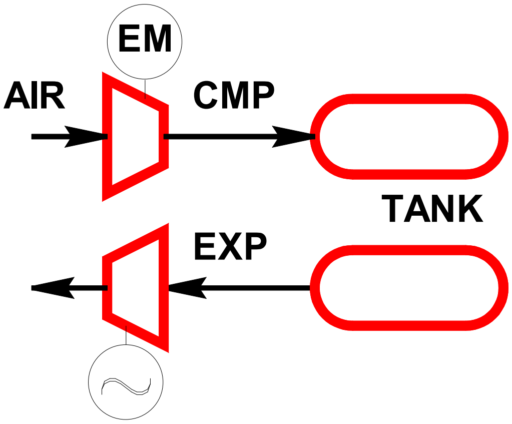

Figure A-IIS.37

CAES was known for a long time and considered not very efficient. Recently, a startup company, LightSail, led by 25-year old Danielle Fong, claims to achieve 70% efficiency (energy in vs. energy out).

Figure A-IIS.38 shows the system proposed by LightSail and called RAES (regenerative air energy storage). Air is compressed (and later expanded) in a reciprocating (positive displacement) compressor-expander CMP/EXP. Water mist is injected to remove the heat of compression (or later to add heat to the expansion). Air and water is separated in phase separator PS. Compressed air is stored in a tank. Water is recirculated. Heat is rejected (or, in expansion step, extracted from) a heat sink such as the atmosphere or a pond. The process is shown on Figure 6 of US Patent 8,247,915 and described in columns 10-11 of said patent.

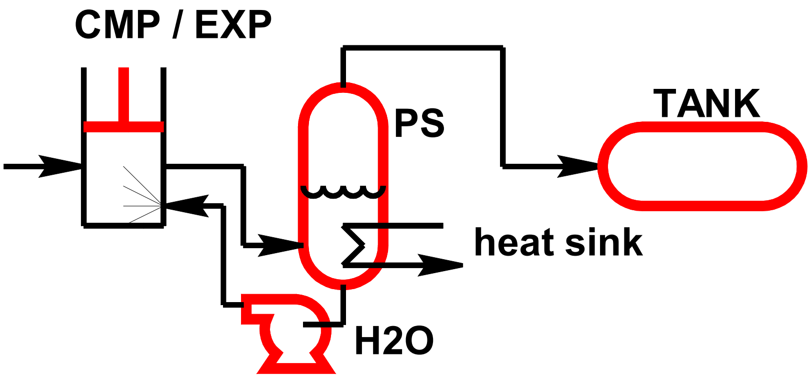

Figure A-IIS.38

Related Ideas

Figure A-IIS.39 shows the use of a DCAC (direct contact aftercooler). A spay nozzle is replaced with packing for improved gas-liquid heat and mass exchange. Can it be used for the process shown on Figure A-IIS.39? Would the process benefit from evaporative cooling of circulating water (a cooling tower)?

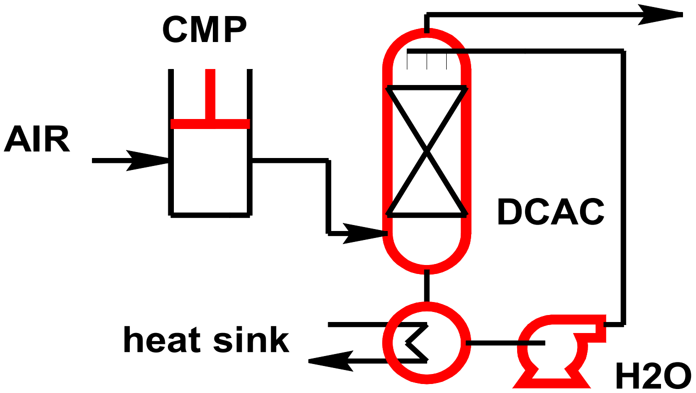

Figure A-IIS.39

Also explore AHAT (Advanced Humid Air Turbine) and water injection in a gas turbine.

Problem Statement

An intermittent energy source (such as solar or wind) produces 1 MW of energy. The assignment is to design a CAES or RAES system (process and apparatus) that will store this energy for three hours with an efficiency of at least 70%. What can be done to improve this efficiency? What's the maximum efficiency that can be achieved? How does the cost compare to other means of energy storage, such as batteries (or, in the case of RAES, conventional CAES)? What will be the effect on cost/efficiency if the energy was to be stored for six hours? Is the solution the same for wind power (the wind blows intermittently 24 hours a day) and solar power (only available during the day, affected by cloud cover)?

References

US Patent 8,247,915
US Patent 8,240,142
US Patent 8,037,677

Links

Danielle Fong (read A Brief Note on Thermodynamics):
http://daniellefong.com/

LightSail (see the diagram):
http://lightsail.com/

Technology Review article on LightSail:
http://www.technologyreview.com/tr35/profile.aspx?TRID=1302

Wired article on LightSail:
http://www.wired.com/wiredenterprise/2012/07/danielle-fong/