

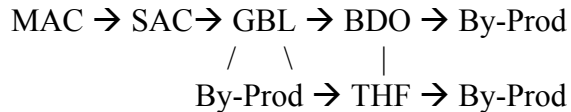
Suggested Design Projects – 2008-2009

1. Maleic Acid Hydrogenation to Tetrahydrofuran (recommended by Wayne Robbins, Consultant (formerly DuPont))

Tetrahydrofuran (THF) is an important monomer used in making polymers and co-polymers with elastic properties such as Spandex[®]. The demand for elastomeric fibers is strong and expected to continue growing.

Your company needs more THF capacity to meet polymer demand. One traditional route is the Reppe process, which uses formaldehyde (HCHO) and expensive acetylene (C₂H₂) as starting materials, and is no longer economically attractive. Your company has an available internal supply of 200 MM ppy (dry maleic basis) of purified maleic acid (40 – 60 wt% balance water).

R&D has developed a new process, which hydrogenates maleic acid (C₄H₄O₄) to THF over a precious metal catalyst in a single reactor. The reaction steps are:



where MAC = Maleic acid, SAC = Succinic acid, GBL = γ -butyrolactone, BDO = 1,4-Butanediol, THF = Tetrahydrofuran, and By-Prod = butanol, propanol, butane, propane, methane.

Most lab work was done in a fixed-bed, plug-flow reactor, but R&D believes that a back-mix reactor with only a vapor product offers many advantages. The intermediates have high boiling points, ~200°C, while the product THF boils at 66°C and would leave the reactor before over hydrogenation makes n-butanol or even butane. To obtain sufficient reaction rates, the reactor operates at 250°C and 2,000 psi. (Reaction details and recommended modeling using ASPEN PLUS will be provided to the design group.)

The reaction also produces several minor by-products consisting of C3, C4 alcohols, and C1, C3, and C4 alkanes. The alcohols need to be separated from the THF product and the alkanes from the recycle hydrogen.

Your company has decided to build a 100 MM lb/yr THF plant along the Gulf coast using this new reactor/catalyst technology. Your design and economic needs include:

1. Reactor and associated equipment for hydrogen gas and liquid intermediate recycle. You should evaluate the possible elimination of a reactor-heat exchanger within the range of the available maleic feed water concentration.

2. Down stream distillation (or other) separation equipment for making product-grade THF.

Product THF must have less than 300 ppm H₂O or other water-equivalent –OH groups. Note that the –OH groups act as chain terminators in the polymerization step. Also, THF forms an azeotrope with water, which complicates the distillation process. The THF product must be 99.95 wt% pure.

H₂ is available in the area by pipeline for 75¢/lb.

Although the polymer plant, the primary THF user, is located on the Gulf coast, THF can be shipped easily by tank, truck, or rail tank car, within the U.S.

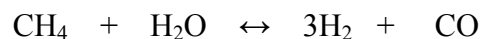
For the economic analysis, commodity bulk prices should be used for the cost of maleic acid and the price of the THF product.

2. Alaskan Natural Gas to Liquid (GTL) using Microchannel Reactors (recommended by John Wismer, Arkema, Inc.)

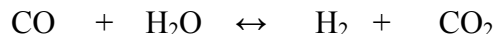
The development of technology to convert methane to useful hydrocarbons has been escalating in recent years. This family of technologies – designated as Gas to Liquids or GTL – can target a variety of end products, such as methanol, gasoline or diesel fuel. As of today, most of the natural gas produced 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 H₂ – 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:

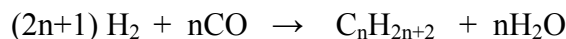


In addition to being highly endothermic, the above reaction is both kinetically and equilibrium limited. Invariably, it is accompanied by the water-gas shift reaction.



The required heat is often supplied by partial combustion of the methane using an air 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 aliphatic hydrocarbons primarily. The target products are paraffinic oligomers in the C5 to C10 range:



However, the synthesis also can produce olefins, alcohols, coke, and carbon dioxide⁷. 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 CO₂ from combustion can be added to the make up the carbon deficit. In most process concepts, the latter approach, called autothermal reforming⁸, 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 platform⁶. 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 than GTL technologies at the gas production capacities of the North Slope⁹. 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 project¹⁰. 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 2Mbps. At this capacity, the TAPS will still have enough capacity to handle the ANWR oil – if it ever gets delivered.

References

1. Wang, Yong et al., U.S. Patent 7,084,180 B2, “Fischer-Tropsch Synthesis Using Microchannel Technology and Novel Catalyst and Microchannel Reactor”, Aug 1, 2006.
2. Tonkovich, A.Y., “Microchannel Process Technology for Compact Methane Steam Reforming”, *Chemical Engineering Science*, **59**, 4819-4824 (2004).
3. Tonkovich, A.Y., “From Seconds to Milliseconds to Microseconds through Tailored Microchannel Reactor Design of a Steam Methane Reformer,” *Catalysis Today*, **120**, 21-29 (2007).
4. Cao, C. et al., “Catalyst Screening and Kinetic Studies Using Microchannel Reactors”, *Catalysis Today*, **125**, 29-33 (2007).
5. Tonkovich et al., U.S. Patent 0033455A1, “Integrated combustion Reactors and Methods of Conducting Simultaneous Endothermic and Exothermic Reactions”, Feb. 19, 2004
6. “A new Offshore GTL production System takes Advantage of Microchannel Reactors”, *Chemical Engineering*, January, 2008.
7. www.pnl.gov/biobased/docs/acs2003presentation.pdf (Battelle presentation showing Fischer-Tropsch results).
8. Parkinson, G., “Gas to Liquids Gain Momentum,” *Chemical Engineering Progress*, May 2005.
9. Alexander’s Oil and Gas Connection, Volume 9, Issue #2- January 29, 2004, “BP and Partner prove Alaska GTL technologies” at <http://www.gasandoil.com/goc/company/cnn40481.htm>
10. See www.arcticgaspipeline.com/GTL.htm.

3. Flexible Manufacturing Facility for Biopharmaceuticals
(recommended by Tiffany D. Rau, GlaxoSmithKline)

Overview

Design a large-scale manufacturing facility to produce a Monoclonal Antibody Biopharmaceutical.

Description

Your company, a large Contract Research Organization (CRO), wishes to expand into contract manufacturing. You are very familiar with the biopharmaceutical market and your expertise lies in biopharmaceuticals obtained from mammalian cell culture systems, specifically Monoclonal Antibodies (MAbs). The pipelines of companies, large and small are filled with biopharmaceuticals. In 2006 alone there were 418 biopharmaceuticals in clinical and non-clinical development with 130 classified as MAbs and 9 already in late stage development (Lubiniecki). Two-thirds of biopharmaceuticals are coming out of companies that have revenues of less than 1 billion dollars. These companies have a need for a Contract Manufacturing Organization (CMO) as they typically do not have the cash reserves to build a manufacturing facility outright.

Currently the worldwide capacity for mammalian cell culture cannot meet the demands of the pipelines. In 2002 it was projected that by 2006 there would be a 450,000 L deficit in the necessary capacity for mammalian cell culture projection based on currently marketed drugs as well as those expected to come on market through 2006 (Mallick).

Your task is to create a facility to produce the next wave of MAb/FAB biopharmaceuticals. For this project, you should plan to produce a humanized monoclonal antibody against TNF-alpha (Tumor Necrosis Factor). The MAb you produce will need to be enzymatically cleaved to a FAB fragment and the fragment needs to be pegylated. You and your team will need to design both the upstream and the downstream processes. Plan to base your facility on a currently manufactured MAb with the understanding that the next generation of MAb/FAB pharmaceuticals will probably be manufactured using advances that are currently coming out of Research and Development Labs. For instance, Lonza's (CMO) current titers are 1-2 grams while they project future titers of 5-10 grams with process improvements. (Citigroup Report. Lonza AG).

Helpful/Interesting Material

Remicade™ and Enbrel™ are both biologicals that target TNF-alpha. The anti TNF-alpha class of drugs has a wide market. For instance, Remicade™ is being used by over 1 million patients across all uses. Remicade™ is currently being used to treat such ailments as rheumatoid arthritis, Crohn's disease, and ankylosing spondylitis.

BioPharm International, BioProcess International, Pharmaceutical Manufacturing, GEN are publications you may find useful.

A shortlist of books will be provided upon request. Seek other books in your library.

Lakshmikanthan, J., *Outsourcing: Biologics Manufacturing: The CMO Advantage*, BioPharm International, February 2007.

Das, R., and K. J. Morrow, Jr., "Progress in Antibody Therapeutics," American Biotechnology Laboratory, August 2006, pp. 8 and 10.

Mallik, A., G. S. Pinkus, and S. Sheffer. "Biopharma's Capacity Crunch," The McKinsey Quarterly: 2002 Special Edition: Risk and Resilience.

Lubiniecki, A. S., "Presentation: Global Industrial Perspective of Novel Biologicals Development," Centocor R&D/Johnson and Johnson.

Datamonitor's Report: Press Release: MAb Sector Growth will Continue to Far Outstrip that of Small Molecules, FierceBiotech, October 12, 2007 www.fiercebiotech.com (obtained 25 September 2008.)

Gerson, D. F., "Paradigm Change in BioManufacturing: Technology is Transforming Manufacturing Options," *Contract Pharma*, May 2008.

4. Butanol by Two-Stage Fermentation
(recommended by Bruce Vrana, DuPont)

Prior to the advent of the petrochemical industry, which made the process uneconomic, acetone, butanol, and ethanol were produced together by fermentation, using one of several *Clostridia* strains. With the growth in interest of biofuels and the increase in price of petrochemicals, fermentation routes to butanol are being revisited by several parties. Butanol is an excellent biofuel, with many advantages over the incumbent biofuel, ethanol. It has higher fuel value, meaning more miles per gallon. It can be blended to higher levels without requiring engine modifications. It has lower vapor pressures than ethanol and comparable octane number.

Dr. David Ramey, of Environmental Energy, Inc. (now ButylFuel, LLC), has patented a unique process that makes butanol without significant amounts of acetone or ethanol in a continuous two stage anaerobic fermentation. The first microorganism converts starch into mainly butyric acid. The acid is transferred to a second fermenter where it is converted by a different organism to butanol. By using two different bacteria, each step in the process can be optimized, resulting in increased fermenter productivity and yield. In 2005, Dr. Ramey drove his unmodified 1992 Buick Park Avenue across the country running on pure butanol made by his process. He claims that butanol can be made for the same cost as ethanol.

Your organization is considering licensing this technology to make butanol for gasoline blending. Your team has been assembled to determine whether the process will be

economical before engaging in any discussions with ButylFuel. Because these negotiations can be sensitive, your management has forbidden any form of contact with anyone at ButylFuel during your design. You may use only information that you can find in the public domain, in the patent, on the Internet, etc. The objective is to obtain a license at the lowest possible price, so you do not want to tip off your company's interest in the process until your engineering analysis is complete.

Because it will compete directly with over 100 fuel ethanol plants in the United States, your process design should draw as many parallels to the typical fuel ethanol process as possible. The references have considerable information on the ethanol process. However, there will be some significant differences in the process from fuel ethanol, since the fermentation is continuous and the product is different.

Design a process to convert corn to make 50MM gallons per year of butanol in the U.S. Corn Belt. Corn costs \$4.00/bushel (56 lbs). Butanol can be sold, according to your marketing forecasts, for \$4.00/gal. As in the ethanol process, unfermented corn is dried and sold as an animal feed coproduct, called DDGS, for \$150/dry ton. Prices are in 2009 dollars. Because of the wild swings in corn prices, you will want to determine the sensitivity of your economics to the corn price. Determine the maximum royalty that you can pay to ButylFuel LLC, in cents per gallon of product, and still earn a 12% IRR on the investment. This will help guide your negotiating team in setting license terms.

The composition of corn may be taken as:

Water	15%
Starch	59.5%
Hemicellulose	4.4%
Cellulose	2.6%
Protein	8.3%
Oil	3.4%
Non-fermentable dissolved solids	6.8%

Approximately 40% of the proteins are soluble. The rest of the solids are insoluble and inert in the system. The oil remains with the insoluble solids and exits the plant in the DDGS. Fuel butanol must be 99.5% pure, with less than 10 ppm aldehydes or ketones.

A good source of physical property data for some of the non-traditional compounds in the process is Wooley and Putsche (1996).

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 inoculum. However, it is well known that fuel plants can not be held to the same sanitary standards as, for example, pharmaceutical plants.

The organisms are naturally occurring strains that pose no known hazards to humans and thus are less stringently regulated than if they were genetically modified. Nonetheless, it would be prudent to design facilities to physically contain live organisms. 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 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 temperature prior to discharge.

Fermentation off-gas will, unlike in ethanol plants, contain a significant amount of hydrogen. 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.

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 strive to meet that benchmark, although you may need to adjust it for the differing fuel value of butanol compared to ethanol. In other words, since a gallon of butanol has more energy than a gallon of ethanol, a more appropriate benchmark might be the BTU required/BTU of fuel product.

As in much of the Corn Belt, water is a big concern at your proposed plant site. The plant will need to be a zero-discharge plant, meaning that all process water is recycled within the plant. The only liquid discharge allowed is the small amount of boiler and cooling tower blowdown required to purge salts. You need to design the process to use the minimum amount of water and purify and recycle essentially all of it. There is no river to which you can discharge effluents. The current benchmark for total water use in a fuel ethanol plant is about 3 gal/gal of product, and you should strive to meet or exceed that benchmark. (Hint – if your water usage is dramatically below the benchmark, you have likely overlooked a major water user on the plant.) You may ignore the small amount of domestic water used on the plant.

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

References

The Renewable Fuels Association web site has a good description of the fuel ethanol process and industry. <http://www.ethanolrfa.org>

A good model of 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 will work 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.

ButylFuel has an informative web site at <http://www.butanol.com> .

U.S. Patent 5,753,474 to Environmental Energy, Inc.

Wooley, R. J., and V. Putsche, "Development of an ASPEN PLUS Physical Property Database for Biofuels Components", NREL/MP-425-20685 (1996).

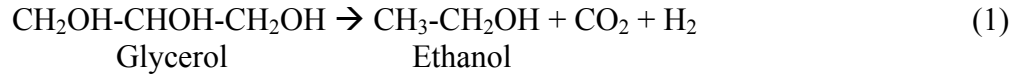
5. Glycerol to Ethanol (recommended by Bruce Vrana, DuPont)

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:



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 inoculum.

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 then disposed of properly. Landfill is adequate for final disposal. Likewise, 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 temperature 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 local 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).

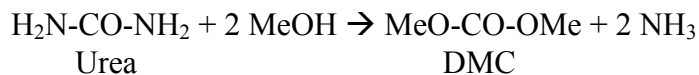
6. New Phosgene-Free Route to Polycarbonates (recommended by Bruce Vrana, DuPont)

Polycarbonates are particularly valued for their optical clarity and impact resistance, and are used in CD, DVD and Blu-ray discs among many other applications. Polycarbonates have historically been manufactured using highly toxic phosgene to make the intermediate dimethyl carbonate (DMC). Besides the hazards of using phosgene, the process must also dispose of byproduct NaCl. A phosgene-free route to DMC would be more economical and environmentally acceptable.

Your company has collaborated with researchers in China who invented a new process to make DMC from urea and methanol, rather than phosgene. The tin-catalyzed methanolysis

of urea is well known in the literature, but plagued by low yield. The new patented catalyst has quantitative yield to useful products in a fixed-bed reactor.

The overall reaction is:



Although not stated in the patent, the only byproduct is methyl carbamate (MC), the half-methanolysis product. If this can be separated from the DMC, it can be recycled to the reactor where the other amine group reacts with methanol to make more DMC.

Your company has assembled your group to develop a process to make DMC from urea, which is manufactured in the adjacent plant. This adjoining plant will also purchase your ammonia byproduct, provided it contains less than 100 ppm of methanol, and will make urea from it.

Design a plant to make 100MM lb/yr of DMC on the U.S. Gulf Coast using the new patented catalyst. Your company currently buys DMC for \$0.40 per pound. Urea is available for \$300/tonne, and methanol costs \$1.00/gal. The adjoining plant will buy your ammonia back for \$300/tonne. All of these prices are in 2009 dollars.

Complicating the process, DMC and methanol form a minimum-boiling azeotrope containing about 70% methanol. Ensure that your simulation of the process uses VLE that properly represents this azeotrope.

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

References

U. S. Patent 7,271,120 to the Institute of Coal Chemistry, Chinese Academy of Sciences and Feicheng Acid Chemicals Co., Ltd.

The azeotrope is reported in Lecat, Ann. Soc. Sci. Bruxelles, 48B, I, 13 (1928) (see Horsley, L.H., *Azeotropic Data III, Advances in Chemistry Series 116*, American Chemical Society, 1973).

7. Toluene Methylation to p-Xylene
(recommended by Bruce Vrana, DuPont)

Growing demand for polyethylene terephthalate has resulted in increased demand for p-xylene (PX), giving rise to the need for new sources of PX. The major source of PX is reformat from oil refineries. Additional PX is made by toluene disproportionation, but that process makes a mole of unwanted benzene for each mole of PX. In contrast, all of the toluene is converted to PX in the methylation process, as shown in the following reaction:



Your company has developed an improved catalyst for this reaction. The patent lists examples with 99.9% selectivity and 100% conversion of methanol at short contact times in a fixed-bed reactor. An excess of toluene is used to improve selectivity to PX, so the unreacted toluene must be separated and recycled back to the reactor. Your group has been assembled to develop the most economical process based on this patent.

Design a process to convert 400MM lb/yr of toluene, which is available at your plant complex on the U.S. Gulf Coast to PX. Toluene is available on your plant site for \$2.50/gal. Methanol can be purchased for \$1.00/gal. PX can be sold for \$0.60/lb. All prices are forecasts by your marketing organization for long term average prices, expressed in 2009 dollars.

The heat of reaction is significant and the reactor design must manage the heat appropriately. The plant design must also consider how to best reach the reaction temperature of 440°C, both in continuous operation and during startup. Because of the size of the plant, energy integration will be important in your design.

The catalyst must be regenerated every 6 months to remove coke that builds up on the surface. This is done by burning it off with air. Your plant design must take this periodic regeneration into consideration.

Your 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. Your 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 7,321,072 to Johnson-Matthey.

8. Design and Control using Stochastic Models of Deposition Reactors
(recommended by Talid R. Sinno, U. Penn)

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. 1 is a schematic representation of some of the different atomic events that are carried out in a KMC simulation [1].

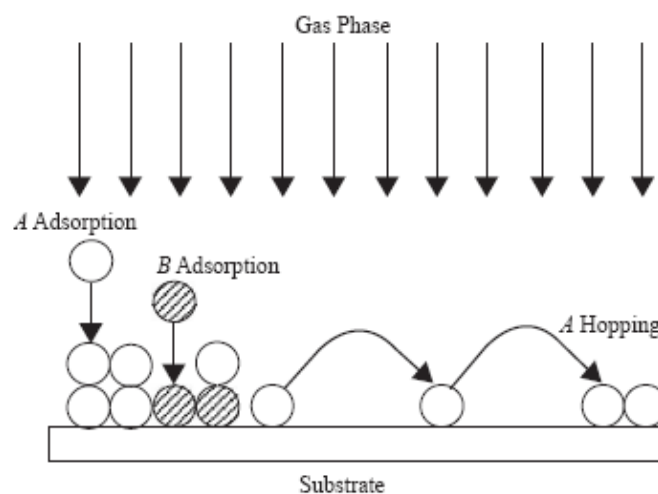


Figure 1. Schematic representation of KMC atomic events on a substrate surface in a two-component system.

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).

9. \$1000 genome challenge for the Archon X Prize for Genomics
(recommended by John C. Crocker, U. Penn)

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. An obvious 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. That is, the prize seeks a factor of 30,000 reduction relative to the 2003 Celera genome! Since then, several firms have started working toward the challenge, including VisiGen, 454 Life Sciences, Ffame, Reveo Inc. and Pacific Biosciences [3]. In early 2007, 454 reported its first human genome, which belonged to James Watson, co-discoverer of the DNA double Helix in 1958 and, ironically, former chief of the HGP. Despite considerable technological progress, the prize remains unclaimed.

This project is to develop a design to claim the Archon X Prize, specifically using the approach chosen by Pacific Biosciences, based on single-molecule sequencing in a zero-mode waveguide [4], as shown schematically in Figure 1. In single molecule sequencing, the genome first is digested into shorter single-stranded pieces, and then these fragments are bound to DNA polymerase enzymes and immobilized on a glass slide under a high magnification microscope. Modern CCD cameras can readily detect the light emitted by single fluorescent molecules (provided they are immobilized). The trick then is to convert the DNA sequence information into a time sequence of optically discernable colored flashes of light. This is where the polymerase comes in: it synthesizes a second strand by adding one complementary nucleotide base at a time. If each of the four DNA nucleotides is prepared with a uniquely colored fluorescent tag, each base added to the growing daughter strand can be unambiguously identified. To avoid a confusing superposition of different colors, the experiment is arranged such that that older tags are destroyed by photobleaching prior to the addition of each new nucleotide/tag. To obtain the immense throughput required, each chamber on the microscope contains hundreds or thousands of fragments having different sequences, which are sequenced in parallel using many different enzyme molecules in the microscope's field of view. Once each fragment species has been sequenced several times in a given data set, it will then be possible to compare them to one another to correct any errors due to incorrect color readout or low polymerase fidelity.

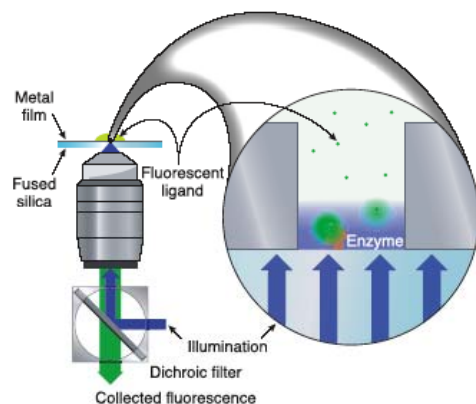


Figure 1. Schematic of microscope detection scheme collecting fluorescence excitation from single DNA/enzyme complexes in zero-mode waveguide wells, from reference [4].

While an exciting technology, such approaches have always suffered from throughput limitations—the tags in solution contribute a troublesome background signal, effectively limiting their total concentration and thus the rate at which bases can be added. A second problem relates to the density at which strands can be packed into a surface before the light from different growing strands starts to blend together due to unavoidable optical diffraction. A team at Cornell developed a major breakthrough called a zero-mode waveguide. It exploits the fact that light will not penetrate through a hole smaller than its wavelength. The prepared a metal mask with such sub-micron holes in it, and put a single polymerase in the bottom of each hole, see Figure. Since light will penetrate a short distance into the hole, looking from the bottom, they could see the DNA strands and their fluorescent tags, but the reservoir of unreacted nucleotides above the mask was invisible. By putting the holes on a closely spaced grid, they were also able to pack the polymerases closer together that they could have with a random arrangement, and were still able to separate the light signal from each molecular complex.

The team will investigate all chemical and physical aspects of the proposed approach, including the kinetics of the polymerase binding, nucleotide addition and photobleaching reactions at the single molecular level, signal to noise level of the fluorescence data, automation of the ‘front-end’ DNA chemical preparation required to create the mixed DNA fragment samples to be analyzed, costing and assembly of the waveguide chambers, computing requirements for image data reduction, error correction, and pattern matching required to reassemble the fragmented sequence, etc. Where possible, operating conditions will be optimized to maximize throughput per unit capital investment. If history is any guide, the winner of the X prize will have spent more on the claim than the purse is worth. For this reason, your approach will be deemed viable for the prize if incremental operating costs per genome meet the \$10,000 target *and* the necessary start-up capital for the prize throughout is less than \$25 million (that is, 2.5X the purse). In addition, the team will also identify two different competing technologies for high-throughput genotyping and perform a bare-bones analysis of their incremental and capital costs to assess their competitiveness.

Since winning an X prize is not an acceptable business model, the team will evaluate the viability of a small biotech start-up company selling full genotyping services to wealthy individuals. The assumed throughput is to be the same as the X prize, 12 genomes/day * 250 days/year = 3,000 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. The financial analysis should seek a significant, positive NPV over a four year time horizon with an appropriate IRR for a biotech startup with venture capital funding. If this financial analysis looks favorable, the team should also estimate the capital requirements to expand their operational throughput to a plausible ultimate demand of 10^6 genomes/year.

References

1. <http://www.knome.com/>
2. <http://genomics.xprize.org>
3. <http://www.pacificbiosciences.com>
4. Levene, M. J., J. Korlach, S. W. Turner, M. Foquet, H. G. Craighead, and W. W. Webb "Zero-mode Waveguides for Single-Molecule Analysis at High Concentrations," *Science*, **31**, 682-686 (2003).

10. Plavix Resistance Point-of-Care Diagnostic Device (recommended by Scott L. Diamond, U. Penn)

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.

NOTE: This project may require laboratory work for characterizing the microfluidic devices.

11. Retrofit of an Isobutane Dehydrogenation Facility to make Propylene from Propane (recommended by Gary Sawyer, Lyondell)

With the decrease in global demand for MTBE, much of the production capacity has been idled or put to other uses. One of the routes to MTBE, isobutane dehydrogenation followed by etherification with methanol, has seen a large decrease in capacity in service. Meanwhile, propylene production from steam cracker olefin units cannot keep up with the demand. This project will investigate the possible retrofit of a butane dehydrogenation plant for propane dehydrogenation to propylene. As such, industry is continuing to bring significant amounts of on-purpose propylene production capacity on-stream. You will determine the new equipment needed, and the limitations (“bottlenecks”) in existing equipment.

A diagram of the process available for retrofit is shown Figure 1. The part of the plant used to make MTBE from isobutylene 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. Considerations can include:

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

The reaction is not completely selective to the desired olefin. At the high temperatures needed, some side reactions include 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 air. The existing regeneration system is able to regenerate 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 \$1.50/gallon and product propylene (60 ¢/lb chemical grade, 62 ¢/lb polymer grade). Also, what price would you have to pay for propane to achieve a target rate of return equal to 15%?

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 for removing 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 flowrates, and the exit concentrations of propylene and ethylene were measured with on-line spectroscopy. The results are in a 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.



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



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 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:



The catalyst is ¼ inch extrudate with an average length of ¼ inch. Bulk density is 60 lb/ft³ and the 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 that shown here.

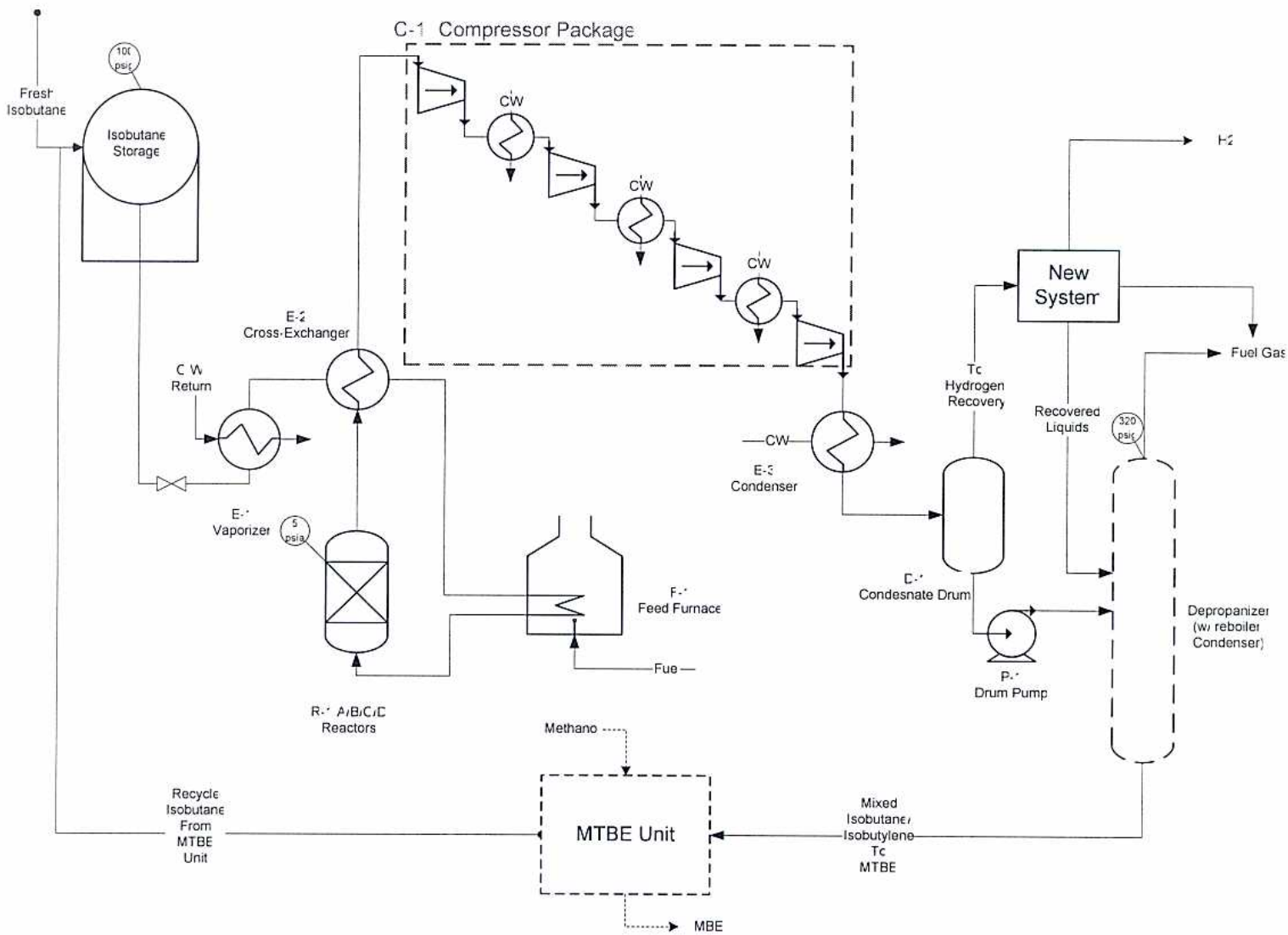


Figure 1

12. Natural Gas Liquefaction using a CO₂-Precooled Reverse-Brayton Cycle
(recommended by Adam A. Brostow, LNG Process Tech., Air Products and Chemicals)

”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 CO₂-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 1, 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 2 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.

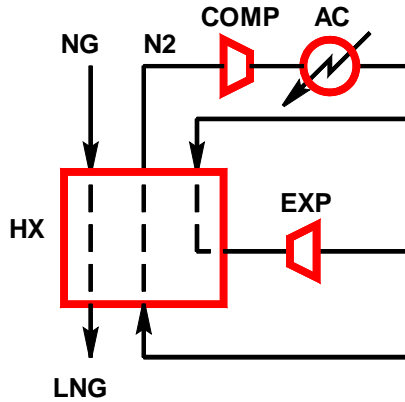


Figure 1 Reverse-Brayton cycle

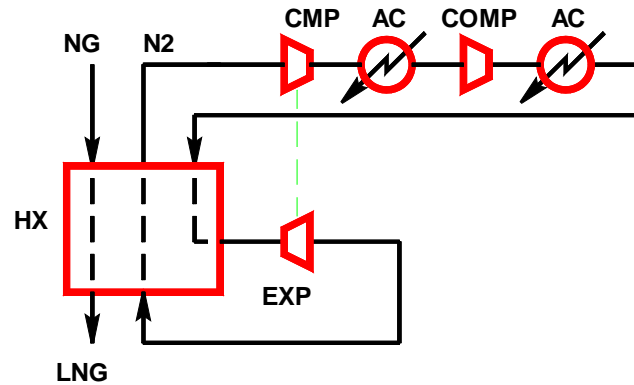


Figure 2. Reverse-Brayton cycle with a compressor-expander

Figure 3 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 4 shows a precooled cycle, where additional refrigerant, such as propane (C3), is condensed, subcooled, throttled, and vaporized. Alternatively, the propane is replaced with CO₂, with multiple temperature levels of CO₂ 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 CO₂ 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 CO₂. While they don't deplete the ozone layer, they have a greater greenhouse effect than CO₂ and are difficult to generate offshore. Your design team is encouraged to investigate methods of producing CO₂ onsite to initially charge the system and to make up for seal losses.

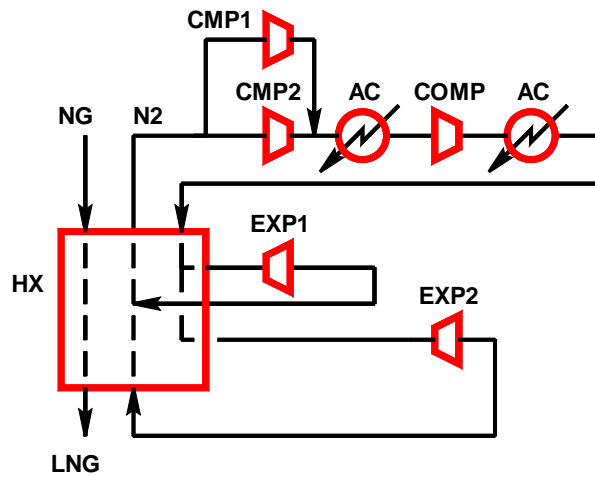


Figure 3. Reverse-Brayton cycle with two expanders

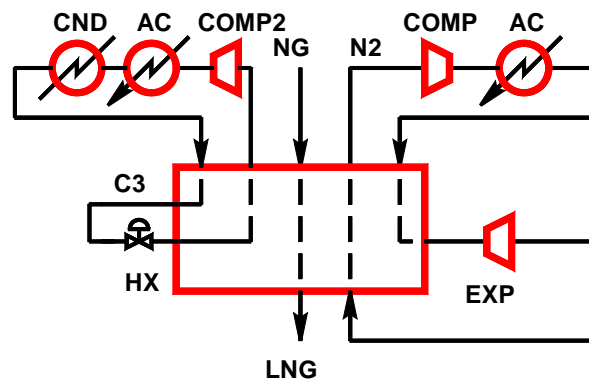


Figure 4. Pre-cooled reverse-Brayton cycle.

Figure 5 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.

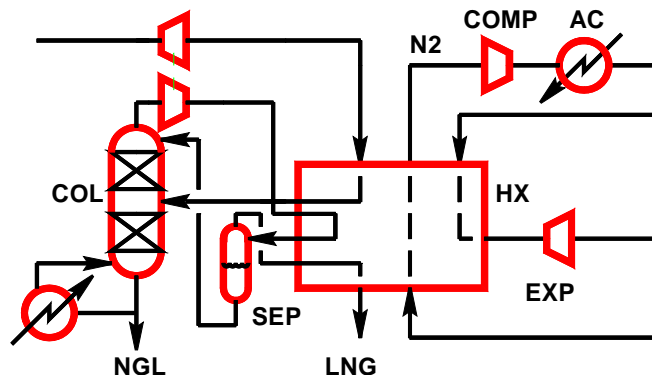


Figure 5. Reverse-Brayton cycle with a scrub column

Figure 6 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°F and at 725 psia containing 4% N₂, 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°F. It is throttled to 18 psia in a product valve and fed to the LNG product separator.

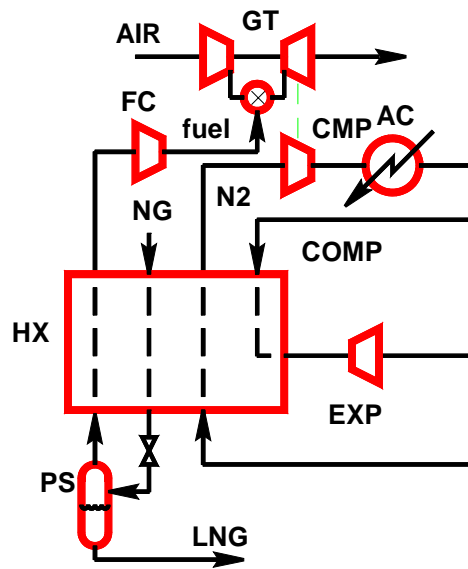


Figure 6. Reverse-Brayton cycle with gas turbine

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 CO₂ 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 pre-cooled by at least one stage of CO₂.

The design team is to determine the limitations of using CO₂ as refrigerant and to determine whether it is necessary to condense CO₂ to achieve a working cycle. The team is also encouraged to find a way to generate CO₂ 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 CO₂ 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 CO₂-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

CO₂ 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.