

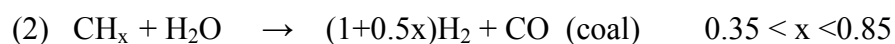
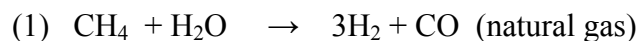
Suggested Design Projects – 2011-2012

1. Alkanes from Pennsylvania Coal and Marcellus Natural Gas by Hybrid Processing (recommended by John A. Wismer, Arkema)

The conversion of natural gas to liquid fuels (GTL) has long been an area of industrial research. Historically, it has focused on converting remote “stranded natural gas” to easily transportable liquids. In fact, a previous design group used a variant of this technology to convert Alaskan natural gas to hydrocarbon liquids⁷. The coal industry has also pursued technologies that convert coal to liquids (CTL)^{6,8}. As a feedstock for liquid fuels, both coal and natural gas are cheaper than crude oil. In the case of natural gas, the cost advantage has increased in recent years. Since 2006, the price of “wellhead” natural gas has dropped from about \$8/MM Btu to <\$4/MMBtu while crude oil has increased from \$60/bbl to >\$80/bbl. At this price, a substantial portion of the “delivered” natural gas price is comprised of transportation and distribution costs. Note that the wellhead price is usually about \$0.25/MMBtu less than the widely quoted NYMEX Henry Hub price. The drop in wellhead price is in large part due to the development of new drilling techniques that have made formerly inaccessible deposits economically attractive to produce. Many of these deposits come from the Marcellus shale – a formation that includes portions of Pennsylvania and West Virginia that also have substantial coal deposits.

Your client is a natural gas producer and a coal mining company that has several leases in Pennsylvania and West Virginia. Most of Pennsylvania’s Marcellus gas comes from either the southwestern or northeastern parts of the state. In the southwestern corner, Greene County has several large coal mines and gas wells in the same vicinity. Your client wants to know whether a hybrid process to convert both coal and gas to hydrocarbon liquids could be economically viable. Hybrid processing offers an elegant solution to one of the drawbacks of the separate conversion technologies: coal as a feedstock for liquid alkanes is too hydrogen-lean and methane is too hydrogen-rich. By hybridizing the processes, it becomes possible to optimize the carbon to hydrogen ratio to produce liquid alkanes at maximum carbon efficiency. By locating the plant near gas wells and coal mines, feedstock transportation costs would be minimized and product would be shipped to nearby U.S. refineries.

The base technology combines steam reforming with Fischer-Tropsch synthesis. The reforming step produces a combination of CO and H₂, known as synthesis gas, in a highly endothermic reaction:



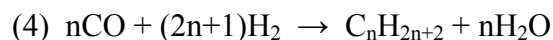
The values of x in Eq. (2) are is on the low side for anthracite and on the high side for bituminous coals. For coal, the water-gas shift reaction is used to enrich the gas in H₂ relative to CO:



The optimum H₂/CO ratio for Fischer-Tropsch (FT) synthesis is about 2:1. Of course, the shift reaction unfortunately degrades some carbon to carbon dioxide. The use of natural gas as a co-feed limits the shift-reaction carbon loss to that which naturally occurs in the reformer.

Hybrid processing has been an area of academic research for some time, but there is no agreed-upon best way to introduce the natural gas into the coal-based process. In one approach, carbon dioxide from the coal gasification reacts with the natural gas.¹ In another, the gas is added to post-treat the liquid effluent of the coal-based FT reactor.³ Another concept combines the coal gasification with natural-gas reforming in a single shell-and-tube unit wherein the heat required for gas reforming is supplied by the hot gases from coal gasification.² Also, the coal and gas can be mixed at the reformer inlet with the reforming reactions at the same conditions.⁴ A variant of this approach is to introduce oxygen into the reformer.⁵ The latter approach, sometimes called autothermal reforming, uses partial oxidation to supply much of the heat required for the reforming reaction. Furthermore, the coal char can have a catalytic effect that precludes the need for a precious-metal reforming catalyst. You are not expected to carry out a detailed analysis of every option. However, you should understand them sufficiently well to make and defend a rational decision on the choice of technology.

The Fischer Tropsch chemistry is as follows:



Also, the evaluation should use the best available technology in its FT processing scheme. For example, the 2009 design group used micro-channel reactors for its FT reactor. This concept might also be applicable to the FT section of the hybrid processing scheme.

The Southwestern PA gas wells are in close proximity to productive bituminous coal mines – and less than 300 miles from the Ohio refineries. The railroad infrastructure of the mine can be used for shipping finished product.

Two simplifying assumptions regarding this process have been specified by your client. Whereas much academic research includes biomass as a potential feedstock in hybrid processing schemes, your client is only interested in coal and natural gas. Furthermore, much of the academic research includes carbon dioxide recycle and/or sequestration as a part of the process simulations. Hybrid processing already offers better carbon efficiency and decreased CO₂ emissions compared with conventional coal-to-liquids processing.

Your client is not interested in processes that involve CO₂ sequestration or non-economical CO₂ recycles.

Your plant should be sized for at least 15,000 bbl/day of hydrocarbon liquids that will be available as a feedstock to the Ohio refineries.

References

Hybrid Processing

- 1) Sudiro, M., and Betucco, A. "Production of Synthetic Gasoline and Diesel Fuel by Alternative Processes using Natural Gas and Coal: Process Simulation and Optimization", *Energy*, **34**, 2206-2214 (2009).
- 2) Adams, T. and Barton, P, "Combining Coal Gasification and Natural Gas Reforming for Efficient Polygeneration," *Fuel Proc. Tech.*, **92** (2011).
- 3) Baliban, R., Elia, J., Floudas, C. A., "Toward Novel Hybrid Biomass, Coal, and Natural Gas Processes for Satisfying Current Transportation Fuel Demands, 1: Process Alternatives, Gasification, Modeling, Process Simulation, and Economic Analysis," *Ind. Eng. Chem. Res.*, **49**, 7343-7370 (2010).
- 4) Cao, Y., et al., "Synthesis Gas Production with an Adjustable H₂/CO Ratio Through the Goal Gasification Process: Effects of Coal Ranks and Methane Addition" *Energy & Fuels*, **22** (3), 1720-1730 (2008).
- 5) Wu, J., Fang, Y., Wang, Y. "Production of Syngas by Methane and Coal Co-Conversion in Fluidized Bed Reactor," *Energy & Fuels*, **19** (2), 512-516 (2005).

Coal-To-Liquid Processing

- 6) Bellman, D., et al., "Coal-to-Liquids and Gas,"
[www.npc.org/study_Topic_Papers/18-TTG-Coals to Liquids](http://www.npc.org/study_Topic_Papers/18-TTG-Coals%20to%20Liquids).

Gas-To-Liquid Processing

- 7) Hammond, J., et al., "Alaskan Natural Gas to Liquids (GTL) using Micro-channel Reactors," Univ. of Penn Design Project, SEAS Library (2009).

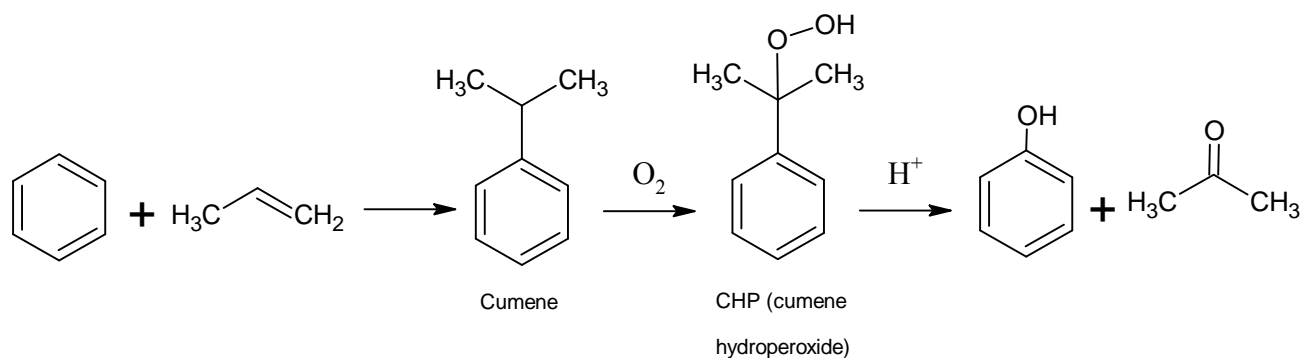
Other

- 8) Schwartz, M., "Local Company to Buy Liquid Coal,"
http://www.ultracleanfuels.com/articles/Lancaster_062506.htm (Note capacity and capital cost).

2. Direct Route to Phenol From Benzene (recommended by Bruce M. Vrana, DuPont)

Phenol is a major chemical intermediate used in a variety of other products. Phenolic resins are used in a wide range of products, including printed circuit boards. Phenol is a raw material to make polycarbonate, used in CD and DVD discs. Phenol can be converted to caprolactam and ultimately nylon-6, or to adipic acid and ultimately nylon-6,6, used for fibers and engineering polymers. There are a wide variety of other applications for this versatile intermediate.

Phenol is conventionally made from cumene using the following chemistry:



This route has several drawbacks. Growth in demand for propylene has exceeded the growth in supply, driving propylene prices higher. Also, one mole of acetone is made per mole of phenol. The acetone must be sold at a reasonable price to have favorable economics on making the phenol. Although acetone has numerous uses, phenol producers often have difficulty selling the byproduct at an attractive price. Effectively, this process converts high-value propylene into low-value acetone. In fact, although you could sell more phenol, your company has decided not to expand phenol capacity when acetone is produced as a co-product.

A team of chemists at the Council of Scientific and Industrial Research (CSIR) in New Delhi has recently patented a direct process from benzene to phenol, using hydrogen peroxide, a chemical which your company also makes in large quantity. While other companies have patented similar chemistry, they have all been plagued by yield loss to over-oxidized byproducts which have no end use. The team in India has measured 53% benzene conversion and 100% selectivity to phenol.

Your company is considering licensing this technology. Your team has been assembled to determine whether the process will be economical before engaging in any discussions with CSIR. Because these negotiations can be sensitive, your management has forbidden any form of contact with anyone at CSIR 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 don't want to tip off your company's interest in the process until your engineering analysis is complete.

Design a process to make 500MM lb/yr of phenol from benzene at your plant complex on the U.S. Gulf Coast. Benzene is available on site for \$0.40/lb. Hydrogen peroxide is also available on your site for \$0.30/lb. Phenol is worth \$0.80/lb to your company. All prices are forecasts by your marketing organization for long-term average prices, expressed in 2012 dollars.

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 approaching CSIR to discuss a license. 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. 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 negotiations are successful, you will be there for the plant start-up and will have to live with whatever design decisions you have made.

Reference

U. S. Patent 7,586,014, September 8, 2009, assigned to Council of Scientific and Industrial Research

3. Cellulose to Coke Bottles (recommended by Bruce M. Vrana, DuPont)

Coca-Cola is promoting what they call a PlantBottle, made from partially renewably sourced polyester. Normal soda bottles (and many other things) are made from polyethylene terephthalate (PET), with both the terephthalic acid and ethylene glycol (EG) monomers coming from fossil sources. PlantBottle uses EG made from fermentation ethanol that is dehydrated to ethylene and then converted to the glycol, which takes two chemical steps and is relatively expensive. And most fermentation ethanol is made from food sources, raising the issue of "food vs. chemicals."

Researchers at the Dalian Institute of Chemical Physics in China, however, have recently patented a direct route from cellulose to ethylene glycol. Their catalyst gives up to 100% conversion of cellulose with mass yield of EG of up to 69%. The EG from their process would be both renewably sourced and produced from non-food biomass, making it more attractive from a sustainability viewpoint.

Your company is considering licensing this technology. Your team has been assembled to determine whether the process will be economical before engaging in any discussions with the Dalian Institute. Because these negotiations can be sensitive, your management has forbidden any form of contact with anyone at Dalian 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.

Unfortunately, the patent does not provide quantitative information on all of the byproducts. Pay careful attention to the definition of the yield in column 5 of the patent. Hexitols are the only byproduct quantified. You may assume that the hexitols are a mixture of equal amounts of sorbitol and mannitol. You may separate and purify those from the other materials in the reactor product, if you wish, as they would be valuable co-products.

Design a process to make 100MM lb/yr of ethylene glycol from cellulose. You can site your plant anywhere in the contiguous United States and use whatever source of cellulose you wish. However, you are encouraged to consider using an on-purpose energy crop such as switchgrass. Although not currently grown commercially at any significant scale, various studies have shown that switchgrass can be produced and sold in agricultural areas at costs as low as \$50/dry ton at the farm. Genera Energy in Tennessee is among those promoting switchgrass farming. You are also encouraged to consider locating the plant near where the feedstock is produced. You need to estimate the cost of delivering the feedstock from the source to your site, which may help guide your decision on siting the plant. Obviously, a sensitivity analysis on the feedstock price would be an important component of your economics.

Of course, cellulose is not the only component in feedstocks such as switchgrass. You will need to make reasonable assumptions about the fate of other components during the reaction, such as hemi-cellulose, lignin, and ash. Test the sensitivity of your plant design and economics to your

assumptions. You might wish to make two very different assumptions and determine the impact on your design and profitability.

Cellulose-based ethylene glycol can be sold for \$0.50/lb. Your main product and any co-products will need to meet normal specs. All prices are forecasts by your marketing organization for long-term average prices, expressed in 2012 dollars.

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 approaching CSIR to discuss a license. 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.

Your 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. Your plant design must also be controllable and safe to operate. Remember that, if the negotiations are successful, you will be there for the plant start-up and will have to live with whatever design decisions you have made.

Reference

U.S. Patent 7,960,594, June 14, 2011, assigned to Dalian Institute of Chemical Physics [China].

4. Ethylene from Ethanol (recommended by Bruce M. Vrana, DuPont)

Ethylene is conventionally produced from fossil-fuel feedstocks such as ethane or naphtha in huge, expensive ethylene crackers. Typical crackers produce 1 million tonnes of ethylene per year and cost over a billion dollars to build. The ethylene market is large and growing worldwide. The industry needs about 5 million tonnes per year of new capacity by 2030 in the U.S. alone. Ethylene is one of the basic building blocks of the chemical industry, going into a wide variety of products, including polyethylene, polystyrene, ethylene glycol, and PVC.

To reduce your company's dependence on fossil fuels, your team has been assembled to design a plant to make 1MM tonnes of ethylene per year from ethanol, made by fermentation of renewable resources. The goal is to be cost competitive with fossil ethylene while reducing greenhouse gas emissions.

Ethanol dehydration to ethylene was practiced commercially in the first half of the 20th century in the U.S. and Europe, and in the second half of the century in Brazil and elsewhere, but was abandoned largely with the global expansion of the petrochemical industry. However, with the increase in the cost of, and limited supply of, fossil fuels, and the growing production of ethanol, companies are beginning to consider this technology again.

Ethanol dehydration to ethylene is an endothermic reaction, usually carried out at 300 to 400°C at moderate pressure over an activated alumina or silica catalyst. Ethanol conversion is 98%, and selectivity to ethylene is about 98%. Ethylene must be 99.96% pure to meet polymer grade specs.

There are two different reactor technologies. An isothermal fixed bed reactor can be run at 350°C with a liquid hourly space velocity of 0.2/hr. Catalyst is typically packed in tubes of a heat exchanger, with heating on the outside to maintain isothermal operation. The catalyst must be regenerated to remove coke approximately every 1 to 2 months, so your design should consider this fact. Regeneration takes about 3 days. Most plants built in the 20th century used isothermal technology. (If you can not find selectivity data, you may assume the same product distribution as in the Petrobras patent for adiabatic reactors without steam co-feed at whatever pressure you wish to operate.)

Alternatively, an adiabatic fixed bed reactor can be used, with an inlet temperature of 450°C. Petrobras technology used steam in the feed to solve the coking problem, and catalyst life was about 1 year. The Petrobras patent gives more details.

You may use either isothermal or adiabatic reactor technology, and if adiabatic, you may add steam to the feed or not. You should justify your choice based on economic estimates as well as technical feasibility.

The United States and Brazil produce most of the world's ethanol by fermentation of local agricultural feedstocks. The U.S. industry is almost entirely based on corn, while Brazil uses sugar cane. Process efficiencies in both countries have improved dramatically in recent years, with increasing ethanol production for use in transportation fuels; thus, do not use process or cost data that is more than 2-3 years old. You may locate your plant in either the U.S. or Brazil, using appropriate construction costs for your location, and local ethanol costs and specs.

If you decide to locate in Brazil, one important factor to consider in your economics is that ethanol price increases dramatically during the inter-harvest period, typically 3-4 months of the year when sugar cane cannot be harvested and local ethanol plants shut down. In recent years, Brazil has imported ethanol from the U.S. during this part of the year. Corn ethanol in the U.S. has no such restriction, as corn can be stored year-round. Be sure to include freight to your plant site in the cost of the ethanol.

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 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.

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

References

U.S. Patent 4,232,179, November 4, 1980, assigned to Petrobras.

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

5. **Butadiene from Ethanol** (recommended by Bruce M. Vrana, DuPont)

The discovery and exploitation of large quantities of shale gas in the United States has resulted in large shifts in the petrochemical market in the past few years. Copious quantities of inexpensive ethane in shale gas have increased the amount of ethane used in ethylene crackers. One of the consequences of this feedstock shift is that significantly less butadiene is made when ethane is cracked. The price of butadiene has increased from an average of \$0.60/lb prior to the discovery, to over \$1.60/lb today. This has increased pressure on making butadiene on purpose from other feedstocks.

Prior to and during World War II, butadiene was made from ethanol. The global growth of the petrochemical industry made that route uneconomical. However, with the increase in the cost of, and limited supply of, butadiene from ethylene crackers, and the growing production of ethanol, companies are beginning to consider this technology again. A side benefit is the renewable feedstock, reducing our dependence on fossil fuels.

To take advantage of the long-term price projections for butadiene, as well as ensure supply for your own needs, your team has been assembled to design a plant to make 200,000 tonnes of butadiene per year from ethanol. Assume that the long-term price for butadiene is \$1.50/lb in 2012 dollars. Obviously, test how sensitive your economics are to the selling price.

Little is known today about the process, other than what was published shortly after World War II. The most successful process was the Ostromislensky process, developed and operated by Carbide and Carbon Chemicals Corporation. The reaction occurs in two steps: vapor-phase dehydrogenation of ethanol to acetaldehyde, and the reaction of ethanol and acetaldehyde over a fixed-bed tantalum on silica catalyst to butadiene at 350°C. Optimal conditions for the second step are a 0.6/hr liquid-hourly-space-velocity, and a 2.65:1 molar ratio of ethanol to acetaldehyde. The catalyst must be regenerated by burning off coke at 400°C every 4-5 days, so your plant design must take that into consideration.

The United States and Brazil produce most of the world's ethanol by fermentation of local agricultural feedstocks. The U.S. industry is almost entirely based on corn, while Brazil uses sugar cane. Process efficiencies in both countries have improved dramatically in recent years, with increasing ethanol production for use in transportation fuels; thus, do not use process or cost data that is more than 2-3 years old. You may locate your plant in either the U.S. or Brazil, using appropriate construction costs for your location, and local ethanol costs and specs.

If you decide to locate in Brazil, one important factor to consider in your economics is that ethanol price increases dramatically during the inter-harvest period, typically 3-4 months of the year when sugar cane cannot be harvested and local ethanol plants shut down. In recent years, Brazil has imported ethanol from the U.S. during this part of the year. Corn ethanol in the U.S. has no such restriction, as corn can be stored year-round. Be sure to include freight to your plant site in the cost of the ethanol.

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

References

Corson, B. B., et al., “Butadiene from Ethyl Alcohol,” *Ind. Eng. Chem.*, **41**, 5, 1012-1017 (1949).

Corson, B. B., et al., “Butadiene from Ethyl Alcohol,” *Ind. Eng. Chem.*, **42**, 2, 359-373 (1950).

Stahly, E. E., et al., “Butadiene from Ethanol,” *Ind. Eng. Chem.*, **40**, 12, 2301-2303 (1948).

Kampmeyer, P. M., et al., “Butadiene from Ethyl Alcohol,” *Ind. Eng. Chem.*, **41**, 3, 550-555 (1949).

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

6. **Blood Processing Unit** (recommended by Scott L. Diamond, U. Penn)

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

Sung, Y., Undar, A., and Zahn, J. D., "A microfluidic device for continuous, real time blood plasma separation," *Lab Chip*, **6**, 871-880 (2006).

7. Membranes for Olefin Separations (recommended by Gary A. Sawyer, Lyondell)

Your company is a major producer of membranes used in water purification, natural gas purification, and carbon dioxide removal. Your R&D department has developed membranes for a new market application, that of olefin/paraffin separation. You have been charged with doing a market penetration feasibility study. The market of primary interest is in propylene/propane separation, which is typically done with conventional distillation.

Polymer grade propylene (99.5 wt% propylene) is nearly a 70 million metric ton per year global business, and is expected to grow at 5%/yr. To meet demand, new capacity will be based on steam cracker technology or propane dehydrogenation technology, both of which separate propylene from a mixture of propylene and propane in a distillation operation known as a “C3 Splitter”. The steam cracker feed to the C3 splitter could also be sold as “chemical grade propylene”. The table below shows typical feed rates and compositions for the C3 splitter in a world-scale plant of each technology.

Table 1

C3 Splitter Sizing Basis	Product Rate, thousand Metric Tons/yr	Feed Wt% Propylene / Propane	Feed Condition
Steam Cracker	600	93% / 7%	80°F, 275 psig
Propane Dehydrogenation	500	35% / 65%	150°F, 450 psig

Membranes

Separation of hydrocarbon gases using membrane technology represents an attractive energy-saving opportunity for modern petrochemical facilities. Membrane technology can be more energy efficient for difficult separations than distillation columns requiring high internal reflux. Traditional membranes operate on a principle of size selectivity and allow smaller molecules to permeate through the membrane leaving larger molecules behind. In engineering terms, membranes operate on the principle that the flux rate (mass flow rate per unit area) across the membrane of individual chemical species in a mixture depends on the type of membrane and the pressure driving force.

Your R&D department has developed a novel membrane that has the potential to separate propylene and propane. These results have only been verified at the laboratory scale and the base-case results are contained in the table below.

Table 2 Membrane Data (Hayashi, 1996)

Temperature (°C)	Selectivity (propylene/propane)	Propylene Permeance (g·mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)
100	33	2.9 x 10 ⁻⁹
65	38	1.5 x 10 ⁻⁹
35	46	7.9 x 10 ⁻¹⁰

Using the data provided in the above table and information in the open literature, design a process to meet polymer-grade purity for the two sizing bases above (Table 1). This may incorporate a hybrid system using conventional distillation and membrane technology. Since Table 2 shows a relationship between operating temperature, selectivity, and permeance, determine the optimum operating conditions to maximize profit. Compare capital and energy costs of your design to conventional distillation. Some assumptions in the cost comparison are:

Steam costs \$8/MMBTU

Electricity costs 6 ¢/kWhr

Cooling water costs 10 ¢/Mgal, and is available at 85°F supply, not to exceed 105°F return

Your management would like to know what membrane price to charge (\$/ft²) in order to make this an attractive investment for the end-user. You will also need to consider in your cash-flow analysis the maintenance and replacement costs for your membranes, expected to have a useful life of 2-5 years. Compare your price to commercially available membranes. Do a sensitivity analysis on membrane performance (flux rates and selectivities) as they would affect this market entry price, which will be used to develop targets for the commercial membrane product.

Finally, determine how your membranes might be used in an existing conventional distillation unit as a capacity debottleneck. For this economic evaluation, the steam-cracker clients value polymer-grade propylene at 1 ¢/lb above chemical grade propylene. Propane dehydrogenation clients value polymer-grade propylene at 15 ¢/lb above propane.

References

Hayashi, et al., *Ind. Eng. Chem. Res.*, **35**, 4176-4181 (1996).

Kim, J. H., Byoung, R. M., Jongok, W., and Y. S. Kang, *J. Polymer Sci., Part B: Polymer Physics*, **44**, 1434-1441 (2004).

Baker, R. W., *Ind. Eng. Chem. Res.*, **41**, 1393-1411 (2002).

Chilukuri, et al., *Ind. Eng. Chem. Res.*, **46**, 8701-8709 (2007).

Kookos, I. K., *Ind. Eng. Chem. Res.*, **42**, 1731-1738 (2003).

8. Renewable Acrylic Acid (recommended by Stephen M. Tieri, DuPont)

As a result of climate change, dwindling petroleum resources, material pricing volatility, and the desire for energy independence, there has been significant research and investment in the last decade to develop technologies that reduce energy consumption, improve efficiency, and produce materials and fuels from renewable resources. Government grants and subsidies as well as consumer demand are driving the intense industrial and academic competition to develop bio-based and sustainable materials – with equivalent functionality to the traditional petrochemical derived materials, but derived from renewable sources and with reduced environmental burden.

Acrylic acid is an important building block in the production of many industrial and consumer products, and existing producers have been investing heavily on R&D resources to produce acrylic acid from renewable raw materials. Most acrylic acid is consumed in polymer form, either directly or after synthesis of an acrylic ester. The acrylic 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 super-absorbents, detergents, dispersants, flocculants, and thickeners.

Through its research efforts, your company has developed new and innovative technologies to produce acrylic acid, through conversion of biomass-derived and renewable feedstocks, rather than crude oil or natural gas. Specifically, a research group developed a microorganism (bacteria) which is the catalyst and basis for this bio-based production route to 3-hydroxypropionic acid, which can subsequently be transformed into acrylic acid. As the acrylic acid has the identical structure and functionality of traditional petrochemical-based acrylic acid, it serves as a direct replacement to produce renewably sourced polymers without modifications to downstream equipment or processes. Early developmental successes resulted in supplemental research funding awarded through several government grants, which have provided partial funding for the development and pilot-production programs.

The microorganism and process have been tested across a variety of commercial feedstocks, with no apparent loss in key fermentation performance metrics or final product quality. Successful pilot trials over the past several years produced material from both 200 L and 20,000 L fermentation vessels, and purified it to greater than 99%. Results from pilot-plant operation indicated that product yield, microbiological productivity, separation, and purification, were on-target to deliver cost advantages at commercial scale. Now that the research, development, and pilot teams have succeeded in achieving their milestone targets, corporate leadership is confident in proceeding to the first commercial-scale production facility. When complete, it is expected that this bacteria-based process will produce 75 percent fewer carbon-dioxide emissions than when generating product from oil.

Your project team has been assembled to design the first commercial plant for this new sustainable technology. The business objective is to design a commercial-scale facility to

produce 160,000 MT/yr (metric tons per year) of acrylic acid from a renewable sugar feedstock. The acrylic acid product purity and quality will need to meet or exceed current commercial requirements for polymer grade material, to be acceptable to perspective customers.

As a result of successful collaborations, your company negotiated an agreement with a world leader in agricultural processing to supply sugar to the plant and process for this program. The bio-acrylic acid manufacturing facility will be co-located on a site with one of the partner's existing facilities. Based on your input, the partner will expand either one of its ethanol dry mills in the Midwestern United States, or one of its sugar and ethanol facilities in Brazil to provide sufficient sugar capacity to meet the acrylic acid process requirements. Starch/sugar/carbohydrate supply from the dry mill is expected to be typical of that currently used to supply fuel ethanol fermentations, while the Brazilian facility will supply molasses and cane juice at standard cane industry concentrations. The project includes the design and sizing of the additional biomass processing systems, sugar extraction/concentration processes, and biomass storage facilities. This is necessary to assure that your partner provides a consistent raw-material supply to your new process. However, your company will not be responsible for direct operation of the biomass to sugar conversion equipment and facilities. The acrylic acid plant is expected to have some onsite storage for the 3-hydroxypropionic acid intermediate and final acrylic acid product at a minimum. In addition to raw material economics, your team will need to consider carefully the advantages, disadvantages, potential obstacles, and restrictions for each sugar supply option when making its selection; for example, the sugar-cane crushing season in Brazil is 8-9 months long.) Current market pricing is to be expected for all raw materials, utilities, and product, regardless of location.

Your company intends to use this technology to attract additional investors, industrial partners for both feedstock supply and sustainably branded intermediates and polymers. Your company expects to build and operate this commercial facility, in addition to some future sister facilities, and does not currently plan to license this technology as an additional revenue source. However, your corporate marketing group plans to advertize this technology as a successful example of your company's capability to achieve smaller process and product costs for building and manufacturing, compared to conventionally produced acrylic acid. Additionally, there is a business target for this commercial process to produce bio-acrylic acid 50 cents/lb lower than conventional hydrocarbon-based acrylic acid.

Your plant design is expected to be as environmentally friendly as possible, and to satisfy state and federal emissions legislation. It is expected that the facility will include emission-control equipment as a part of the process design. You should recover and recycle process materials to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified – and the plant design must be controllable and safe to operate. As the process technology integration and design team, you will participate in the start-up and will have to live with any of your poor design decisions.

You will need additional data beyond that given here and listed in the references below. Cite any literature data used. If required, make reasonable assumptions, state them, especially when your design operation or economics are sensitive to the assumptions you made.

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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, SUPERPRO DESIGNER does not handle VLE rigorously, and thus, is not suitable for designing this process.

Web resource for sugar and sugar solution properties (including molasses), with references for items common to the sugar and ethanol industries.

<http://www.sugartech.co.za/matlprop/index.php>
www.ams.usda.gov

9. Renewable Para-Xylene (recommended by Stephen M. Tieri, DuPont)

The international demand for xylene isomers continues to increase steadily, with *p*-xylene in high demand as a key raw material in the bottling, packaging, materials, and fiber industries. Climate change, dwindling petroleum resources, a desire for energy independence, and consumer behavior are driving significant research and investment into the development of technologies that reduce energy consumption, improve efficiency, and produce chemicals and fuels from renewable resources. The disposition of agricultural resources and production to support both this transition from fossil to renewable fuels, while providing food to meet the demands of the increasing global population, is a source of controversy and significant discussion. Additionally, several beverage makers are actively seeking a plant-based route to plastics for their product packaging, to actively demonstrate their commitment to sustainability and the global environment.

Through its research efforts, your company has developed new and innovative technology to convert biomass-derived material into para-xylene, as an alternative to traditional production routes. Because the material from this innovative catalytic technology has the same composition as traditional petroleum-based para-xylene, it can be used directly in current manufacturing processes, or blended with conventional petroleum-based material, and distributed through existing supply chains without equipment modifications or separate shipping containers. In its current state, this technology is flexible to be optimized and modified to convert multiple renewable feedstocks to para-xylene, using a patented catalytic process to convert the plant-based sugars into monomer. In laboratory and pilot-scale testing, the technology has proven to be equally flexible with respect to potential raw materials, and able to accommodate a varying range of feed materials from glucose and sucrose (derived from sugar crops), starches, glycerol, polymers of glucose contained in cellulose (plant-cell walls), and longer chain C₅ and C₆ sugars (such as those contained in hemi-cellulose). Your company's product trials show that the *p*-xylene produced using this technology is suitable for conversion into the polyethylene terephthalate (PET) raw material, purified terephthalic acid.

Your team has been assembled to design the first commercial facility, and to identify the optimal raw material to demonstrate the commercial viability of this new technology, using assumptions identified by your research and business directors. Your directors agree that the biomass options for this first facility should be limited to woody biomass, sugar cane, and corn grain. It's expected that woody biomass can be converted to sugars using standard enzymatic technology developed for the corn and cellulosic ethanol industry and available from industrial enzyme suppliers. However, they have concerns that the additional investment necessary for pre-treatment and enzymatic conversion of the biomass to sugars may restrict the economic viability of the innovation.

Your company recently acquired both corn dry-grind and sugar-cane ethanol facilities, in an effort to proactively provide access to the necessary raw material supplies (corn grain and sugar cane) at market pricing. These facilities are in Nebraska (U.S.) and in the Sao Paulo region of Brazil, respectively. Partnership discussions for woody biomass supply, in

the Pacific Northwestern region of the United States, are currently in progress. This material is expected to be available in Washington State, and in the form of mill residue (but also land clearing debris and forest thinnings). Sugar supply from the dry mill is expected to be typical of that currently used to supply fuel-ethanol fermentations, while the Brazilian facility will supply molasses and cane juice at standard cane industry concentrations. In addition to raw material economics, your team will need to consider carefully the advantages, disadvantages, potential obstacles, and restrictions for each sugar supply option when making its selection; e.g., the sugar-cane crushing season in Brazil is 8-9 months long. Current market pricing is to be expected for all raw materials, utilities, and product, regardless of location.

A key point of the Directors' interest involves the potential similarities and differences between facilities using woody biomass compared to molasses and cane juice, and sugar liberated from corn grain, including but not limited to, capital investment, overall process sustainability, and profitability. Your business director has determined that the process facilities and equipment should produce at a 400 MMTb per year capacity, using the technology documented in the patents, patent applications, and references listed below as an initial basis. Your para-xylene product must meet the minimum industry purity and quality standards for polymer intermediate grade material, as the expected end use is in bio-PET production. Given the recent volatility of petroleum markets and pricing, your marketing organization is unsure if this material will be able to command any premium above market pricing. Therefore, your business director believes sensitivity analyses are necessary to understand the potential exposure to market fluctuations, and any benefit that a market premium could provide.

This technology has potential use in the U. S. Corn Belt, where water is an extremely limited resource and a large area of concern for any potential plant site. Therefore, your plant and process design will need to use the minimum amount of water necessary for the technology, with the goal of being a zero-discharge plant (meaning that all process water is recycled within the plant). 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 this benchmark, regardless of raw biomass source.

Your plant design should be as environmentally friendly as possible, and satisfy the required state and federal emissions legislation. It is expected that the facility will include emission-control equipment as a part of the process design. 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 be controllable and safe to operate. As the process technology integration and design team, you will participate in the start-up and will have to live with any of your poor design decisions.

Undoubtedly, you will need additional data beyond that given here and listed in the references below. Cite any literature data used. If required, make reasonable assumptions, state them, and identify whether your design or economics are sensitive to the assumptions you have made.

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<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.

Web resources for sugar and sugar solution properties (including molasses), with references for items common to the sugar and ethanol industries.
<http://www.sugartech.co.za/matlprop/index.php>
www.ams.usda.gov

10. Microfluidic Production of Depo-haloperidol with a Controlled Release Profile (recommended by John C. Crocker, U. Penn, and Robert Meyer, Merck & Co.)

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 1. 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.

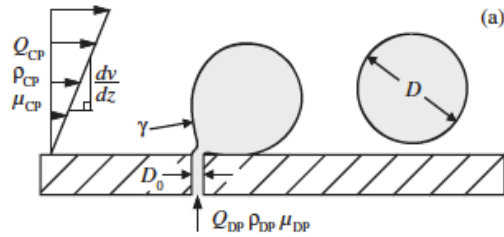


Figure 1: A schematic of the cross-flow membrane emulsification (XME) process, with an oil drop growing while attached to a micropore orifice before eventually being torn away by a shear flow over the plate. Relevant variables are defined in the text.

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.

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11. Gas Turbine Heat Recovery for Reduced CO₂ Emission in an LNG Plant (recommended by Adam A. Brostow, Air Products and Chemicals, Inc.)

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 1 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 through 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.

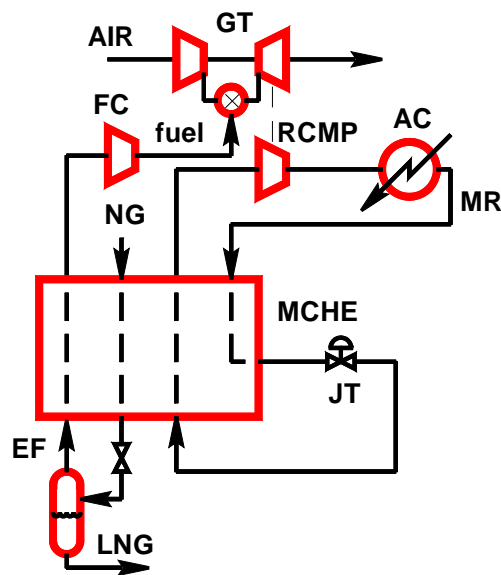


Figure 1

Figure 2 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 CO₂ emissions and larger carbon footprints of such plants.

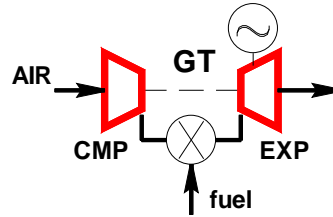


Figure 2

Figure 3 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.

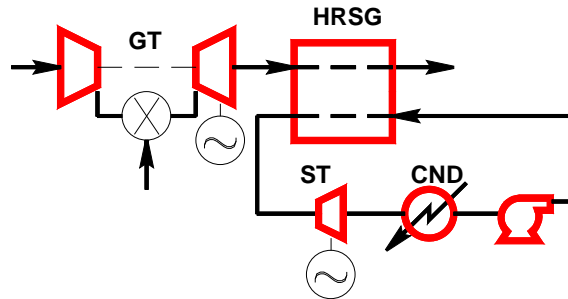


Figure 3

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 CO₂ 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 CO₂ 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 directly 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 CO₂ emissions by employing the combined cycle (Figure 3), 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 equipment.

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.

12. New Environmentally Acceptable Co-solvent for the Reclamation of Co-Solvents (recommended by Leonard A. Fabiano, U. Penn)

The CBE Department recently obtained a powerful software package that CBE students were introduced to in CBE 400. ProCAMD in ICAS 14 is a property-prediction software developed at the Denmark Technical University. Government oversight has ruled out the use of several solvents to be used as cleaning co-solvents. One co-solvent is described below as the currently allowable one. There are always concerns that a regulation could disallow its use, requiring that other solvents be found. These must not be carcinogenic, not be toxic to the environment, and not form azeotropes with the cleaning fluids to avoid difficult separation problems. In this problem, one or more solvents will be found for this application using ProCAMD.

This problem presents the opportunity to make a difference in the future of this process and business, while learning more about molecular structure design and the principles of batch distillation.

Your company, Creative Trollers of America, has been asked to study and prepare proposals to recover co-solvents and reject the removed oil-water mixture from spent metal-working cleansing fluids. Also, the oil used in machining must impart its lubricating properties so that friction between the moving parts and the contact surface of any cutting tool is reduced (Forbes, 1943). From an OSHA perspective, a high percentage of water in the emulsion prevents the oil from misting into the atmosphere, exposing operators to potentially hazardous materials. As a result, the part being machined has a working surface that contains an inorganic contaminant, water, and an organic contaminant, oil. The overall cleansing strategy is to use an alcohol to remove the water and an organic solvent to remove the oil. Examples of the machined metal parts are those cut to a specific geometry – bearings, drawn tubes, or coils for heat-exchange equipment. The aircraft and rocket production industries also utilize large baths to clean oil and water from the parts' surfaces.

Mineral and vegetable oils are used in machining emulsions. The most commonly used mineral oils are refined paraffinic (C_nH_{n+2}) or naphthenic (C_nH_n) oils (Natchman and Kalpakjian, 1985), which are characterized by API gravity, viscosity, and flash point. Vegetable oils, on the other hand, consist of fatty acids and are used for their profound effect on the surface tension of water. Oleic acid or 9-octadecenoic acid ($C_{18}H_{34}O_2$) is a good example of a vegetable oil used in machining and will be used in this project.

In recent years, environmental concerns and laws have changed the choices of solvents. As a result, TCA and CFC-113 are now banned substances and have since been replaced by regulated solvents such as perchloroethylene (PCE), trichloroethylene (TCE), HCFCs, and volatile methyl siloxanes and terpenes in aerosol form. However, with ever growing legislation, cleaning manufacturers and their customers often find managing regulated solvents like PCE and TCE a difficult task riddled with headaches. Thus, there has been recent interest in the use of non-regulated and/or more environmentally-friendly solvents like n-propyl bromide (NPB) and inseparable isomers of methoxy-nonafluoro-butane ($C_4F_9OCH_3$) or hydrofluoroethers (HFEs). NPB is a non-regulated solvent with cleaning

capabilities similar to TCE and PCE. However, it is not clear how long NPB will remain a non-regulated substance. HFEs, on the other hand, are a class of compounds marketed by the 3M Company (1996 – reference not available) more as rinsing agents than as solvents since they are often mixed with trans-1,2-dichloroethylene and sold in a variety of non-azeotropic and azeotropic co-solvent cleaners. Isopropyl alcohol (IPA) has long been an accepted cleaning reagent in the medical industry and for water removal.

Nowadays the cleansing systems are vapor-phase degreasing processes. That is, the contents of the degreasing equipment are maintained at typically 180°F, depending on the co-solvent, in this project case. The degreasing equipment ranges from 4 to 80 feet long, with the smallest unit holding 100 gal of co-solvent and the largest unit containing four 4,600 gal truck loads. The vapor rises to envelop the metal parts and remove the oil from the metal surfaces. The effluent vapor rises to chillers for condensation, with the liquid recycled. The metal parts are cleansed while moving through the process at an elevated temperature, emerging completely dry. The design and operation of the degreasing equipment to minimize or eliminate fugitive emissions is the responsibility of the cleaning system operations organization. Note: the reclamation company does not operate the onsite cleansing equipment. Their only goal is to clean up and resell the solvents.

The co-solvent mixture is initially at 56 mol% IPA and 44 mol% NPB, as this mixture has been determined to have superior characteristics/properties. During processing, after the co-solvent composition is reduced to 85 mol%, with 7.5 mole% oil and 7.5 mole% water, the resulting mixture is ready to be processed. Note that the initial clean co-solvent is always at a fixed purity. It is expected that the paraffinic oil, oleic acid, can be removed completely. Your company must decide the extent to which the water content can be lowered – to keep the equipment and operating costs reasonable. However, the water composition should not exceed 2.5 mol%.

Design a process to recover the co-solvent, NPB/IPA, from a degreasing system that requires one tank truck (4,600 gal) of fresh co-solvent. Typically a batch of co-solvent can be used for two weeks before the threshold of 15 mol% oil/water is reached. Note that the return mixture will contain 15 mole% oil/water. Your management requests that you consider a batch process, a continuous process, and a combination of the two. Determine the processing capacities at which the batch and continuous processes are economical. Does the combined process offer economic advantages? Is there a capacity below which only batch processing should be considered?

The Parts Cleaning Technology Company in Ciniminson, NJ, should be of interest. Its facility provides fresh co-solvent to customers. It collects and sends the recycled mixture to its complex in Charlotte, NC, for recovery. It also has a facility in Bowling Green, KY, that manufactures cleaning equipment. Its website provides much general information: <http://www.partscleaning.net/equipment.htm>.

Given this collection point in Ciniminson, NJ, it seems clear that many local users need their co-solvent to be reclaimed. Suggest a good location for our proposed tolling operation. Steam, electricity, and cooling water utilities are needed. A location in the

vicinity of a steam generation plant for the purchase of steam “over the fence” would be preferable to buying a steam-generation facility. It should be possible to make the other utilities available on site, along with process air and nitrogen (purchased).

Parts Cleaning Technologies sells NPB at \$2.10/lb. IPA prices in bulk need to be found. At this point, we anticipated that the oil recovered will be incinerated. It likely contains some solid residues. You can assume fuel value for the oil.

References

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