

Suggested Design Projects – 2019-2020

1. Rare Earth Element Recovery from Solid Wastes using Biolixivants (Recommended by Gary Sawyer, CDI Corporation)

Rare earth elements (REE) find important uses in permanent magnets for wind turbines and electric vehicles, high efficiency lighting, and refinery catalysts¹, to name a few applications. They consist of the Lanthanides in the periodic table, plus Scandium and Yttrium.² The term “rare” is somewhat of a misnomer, as they are more common than gold, silver, and other important metals, existing in concentrations from 1-100 ppm overall in the earth’s crust, depending on the element.³

A threshold for economic recovery of REE is around 300 ppm⁴. China has dominated the global production of REE in recent history⁵, although the US has in the past produced REE from the Mountain Pass Mine in California³. Note that the China and US REE ores differ significantly in composition³. The individual rare earth elements are separated and sold either as metals, or metal oxides (REO)².

With production so heavily concentrated in one country, some novel approaches have been proposed to recycle REEs from solid waste streams.

More broadly, a hydrometallurgical technique to recover metals from ores is to leach the desired metal using a “lixiviant” – such as sulfuric acid – as an aqueous extraction agent with a targeted pH. The recovered, dissolved metals in the leachate are then separated and purified using several steps⁶.

Researchers at Idaho National Laboratories (INL) have recently investigated biologically sourced “biolixivants” using a strain of *Glucanobacter oxydans*. They studied its application to REE recovery from refinery fluid catalytic cracker (FCC) catalyst, and provide a technical and economic assessment.^{7 8} They are investigating a similar application to phosphogypsum (PG)⁹, a waste product from phosphate production for the fertilizer industry¹⁰. Phosphates are produced in the US in Florida, Idaho, North Carolina, and Utah¹¹. Phosphate mining produces more of the valuable Yttrium and Neodymium¹⁰, than the FCC catalyst which produces primarily Lanthanum and Cerium⁷.

¹ U.S. Department of Energy, Critical Materials Strategy, December 2011
https://www.energy.gov/sites/prod/files/DOE_CMS2011_FINAL_Full.pdf

² USGS Fact Sheet 087-02, “Rare Earth Elements – Critical Resources for High Technology”
<https://pubs.usgs.gov/fs/2002/fs087-02/>

³ Ibid., Figure 3. <https://pubs.usgs.gov/fs/2002/fs087-02/>

⁴ Herbert W. Cooper and Bodo Albrecht, “21st Century Products: A Challenging Economic Future”, Chemical Engineering Progress (AIChE), September 2018

⁵ Hobart M. King, “REE- Rare Earth Elements and their Uses”, <https://geology.com/articles/rare-earth-elements/>

⁶ SRK Consulting, S. Alternative Technical Economic Model for the Mountain Pass Re-Start Project;
<https://www.sec.gov/Archives/edgar/data/1489137/000095012310065239/d74323fwp.htm>

⁷ Vicki S. Thompson, et. al., “Techno-economic and Life Cycle Analysis for Bioleaching Rare-Earth Elements from Waste Materials”, ACS Sustainable Chem. Eng. 2018, 6, 1602–1609

⁸ https://pubs.acs.org/doi/suppl/10.1021/acssuschemeng.7b02771/suppl_file/sc7b02771_si_001.pdf

⁹ Paul J. Antonick, et. al., “Bio- and mineral acid leaching of rare earth elements from synthetic Phosphogypsum”, J. Chem. Thermodynamics 132 (2019) 491–496.

¹⁰ For a representative composition, see: Patrick Zhang, et. al., “Rare Earths Occurrence in Florida Phosphate Ore and Their Fate during Mining and Chemical Processing”, https://dc.engconfintl.org/phosphates_viii/38/

¹¹ USGS National Minerals Information Center, Phosphate Rock Statistics and Information, Minerals Yearbook 2016, Table 3, <https://www.usgs.gov/centers/nmic/phosphate-rock-statistics-and-information>

Project Scope

Your design project is to design the fermentation process to produce the biolixiviant, and the extraction process to recover REE in aqueous form, for the two waste streams as studied in references 7-9:

- Using FCC waste catalyst from a typical catalyst processing facility (student research to determine appropriate size)
- Using PG waste from a phosphate mine (see reference 11)

Your deliverables for the project must include:

- A flowsheet showing the material balance, major equipment, and energy consumption for each case above.
- A discussion of the scale and location chosen as the base design for each case.
- A discussion of key design decisions, such as conditions for the bioreactor and recycle of biolixiviant to the extraction process.
- A discussion of the safety considerations, and to the extent possible, characterization of wastes and their dispositions. Consider issues such as:
 - Spent biologic materials
 - Trace hazardous metals, including possible trace radioactive elements
 - Odor abatement, if open pit leaching is used
 - Wastewater disposal
- A comparison of the economics of FCC versus PG as sources of REE, including sensitivities to the price of individual rare earths and cost of nutrients.
- To the extent possible, compare costs of recovery using biolixiviant versus conventional extraction using inorganic acids. Conventional extraction would be determined from student literature study.

The battery limits include storage of any nutrients / feedstock for biolixiviant production, and storage facilities for recovered REE. The separation of individual rare earths is out of scope, although some discussion would be beneficial.

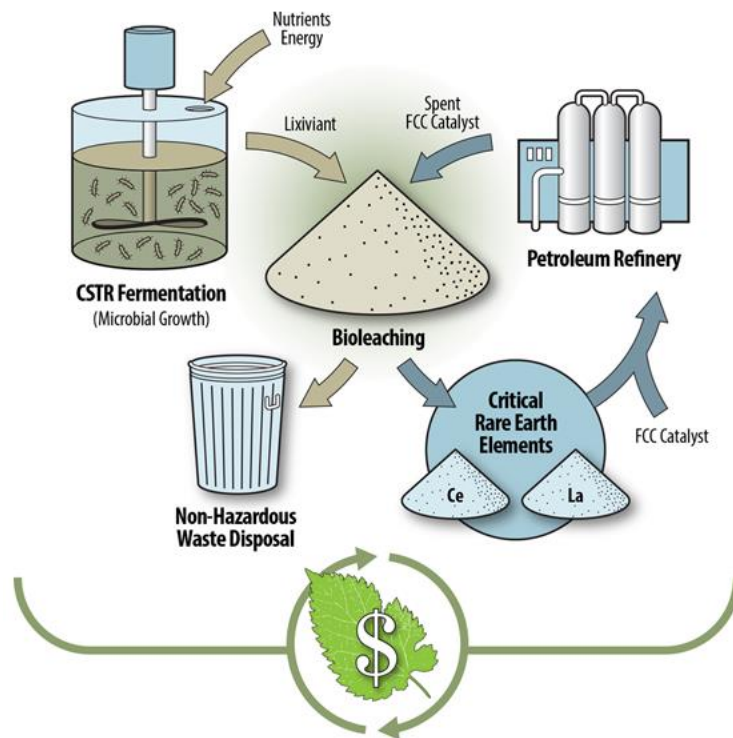


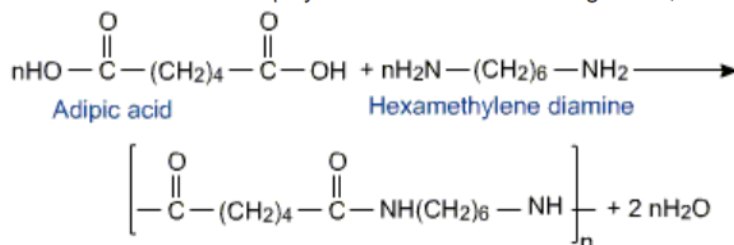
Figure 1. Biolixiviant for REE recovery from FCC catalyst, from Abstract in reference 7

2. Nylon Manufacturing Facility Design (Recommended by P. C. Gopalratnam, Consultant – formerly DuPont, INVISTA)

Project Background

Nylon 6,6 is a co-polymer produced via step-growth polymerization of adipic acid (AA) and hexamethylene diamine (HMD). Nylon 6,6 was invented in 1935 by Wallace Hume Carothers at the DuPont Experimental Station in Wilmington, Delaware. The two monomers each have 6 carbon atoms giving Nylon 6,6 its name, not to be confused with Nylon 6, made from a single monomer, caprolactam. Nylon 6,6 is a widely used polymer in a variety of industries, including textiles. The reaction chemistry is illustrated below: [1]

Here the polyamide Nylon-66 is formed by heating the reactant mixture under pressure and the process has been developed so that the molecular mass of the polymer is controlled in the range of 12,000 to 20,000 amu.



The purpose of this project is to provide a preliminary design of a Nylon 6,6 grassroots manufacturing plant in Kentucky using a continuous polymerizer (CP) and a set of batch autoclaves as 40%, 60% nominal annual capacity respectively for a total output of 150 MM pounds per year. Moreover, for profitability analyses assume 75% of the product goes into the polymer market as pellets and the remaining 25% as carpet fiber. If nylon 6,6 fiber prices are not available, assume a 30% price premium for the fiber market over polymer sales.

Process Description

Nylon 6,6 is synthesized by polycondensation of HMD and AA (Patent No. EP 2460839 A1, 2010). Equivalent amounts of HMD and AA are combined with water in a pre-polymerization reactor. This is crystallized to make nylon salt, which has precisely stoichiometric equivalents. The nylon salt goes into a reaction vessel where polymerization takes place either in batches or continuously (your process design includes both). Removing water drives the reaction toward polymerization through the formation of amide bonds from the acid and amine functions. The molten nylon 6,6 can be extruded and granulated as pellets or directly spun into fibers by extrusion through a spinneret (a small metal plate with fine holes) and cooling to form filaments [2].

The pH of the starting salt solution inside the reactor is of significant importance in the final product quality and must be controlled between 7.0 and 7.5 (Patent No. EP 2460839 A1, 2010). Increasing the pH requires more HMD and vice versa.

Design Requirements

Your task is to prepare a complete economic analysis for building a grass roots plant to produce the needed annual production of Nylon 6,6. You may use any publicly available resources necessary to complete your design including patents, technical reports, literature or other resources. Not all public sources are reliable, however, so you need to consider critically the information and the source before relying on it.

The project will incorporate a wide range of aspects related to chemical process and product design, e.g. flow sheet synthesis and ASPEN simulation, heat and mass integration for resource conservation, facility siting, process optimization, process economics, and environmental, health and safety related issues.

Project Objectives

Your objective is to design and analyze an industrial process to produce Nylon 6,6 using a CP and a bank of batch autoclaves along with extruders and spinnerets for the task at hand detailed above. The final process will generate not only product streams, but also waste streams. The disposition of these waste streams must be considered both in the design and in the economic analysis to comply with the local, state and federal EPA and other regulatory standards.

Furthermore, due to changes in market conditions, customer demands, etc., you need to design your process/equipment for 100% as well as a turndown case of 67% capacity.

You must keep safety, sustainability and controllability in mind as you prepare your design, so be sure to include environmental, health and safety considerations in your report. This system uses raw materials and generates products that are hazardous and/or flammable. What are the process risks and how can those risks be mitigated? How will you set design pressures and temperatures for your process equipment? Can the principles of inherently safe process design be used to reduce the hazards of this process? Are there any special requirements for unsteady-state conditions, such as start-up or shutdown? Include design details for safety relief system, health considerations, environmental considerations and sustainability.

All design choices and changes in direction or scope must be fully justified with reasons explained. Just like a real-world project, you won't always have all the information you need. Therefore, you will be required to make assumptions along the way. Always state your assumptions and reasons for making them. Test the reasonableness of the assumptions, and how critical they are to the feasibility and economics of your proposed design.

References:

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[1] Preparation of Nylon-66 - membrane solutions <http://nylon66membrane.com/Preparation-of-Nylon-66.html>

[2] Nylon 66 https://en.wikipedia.org/wiki/Nylon_66

3. Production of Dimethyl Ether (DME) for Transportation Fuel (Recommended by P. C. Gopalratnam, Consultant – formerly DuPont, INVISTA)

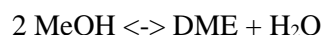
The use of dimethyl ether (DME) as a transportation fuel has been called a path towards near zero particulate emission diesel cars [2], and vehicles. DME can be produced from a variety of sources such as sustainable biomass, municipal solid waste, [3] or CO₂ and sustainable energy supplies [2], as well as natural gas and methanol making it a flexible and unique product with potentially improved environmental and human health impacts.

Design and develop details for a total plant and determine the production cost of DME from methanol. Also include your group's suggestion on incentives to motivate transportation users to switch from low sulfur diesel to DME. DME Fuel Standard composition requirements: (ref ASTM D7901.144734). Evaluate your recommendations to include a risk analysis of technical, business and operational safety.

The plant should be capable of supporting a high volume shipping region consisting of 2,000 trucks (6 mi/gal of diesel x 12 hr/day) traveling at an average speed of 60 mph. Production of DME should meet the minimum demand specified above, adjusting for DME's reported 5.3 miles/gallon fuel economy [17], with slight excess to accommodate variations in truck traffic, and with a turn down of 50%.

The total plant design should include OSBL storage of the raw materials, waste as well as the product in a tank farm in order to facilitate truck-loading spots. Methanol should be considered the feed material for the process. Methanol pricing will be subject to market prices throughout the life of the project and [4] historical prices be found on websites such as www.Methanex.com. You may locate your plant anywhere in the U.S. that has adequate truck traffic, but methanol transportation costs from the nearest MeOH plant large enough to meet your demand needs to be included in your economics. The cost of rail transportation of methanol from the methanol plant to your site can be estimated as (\$0.015 + \$0.0002/mile) per gallon of DME, unless you can find a more accurate value.

You may choose to use any process you wish, and the following information should be considered as only one possible starting point. Clearly explain the rationale for the process you have selected. DME can be produced by a gas phase condensation reaction of methanol using an acid catalyst. The reaction of Methanol to DME is as follows:



It is an exothermic equilibrium reaction catalyzed by an acid. The thermodynamics of Methanol/DME/Water Systems are such that DME and Water will form two liquid phases when MeOH concentrations are low [9] [12]. Separation methods should consider the effects of a possible three-phase mixture in this region.

There are numerous options for the catalyst, but typically solid (heterogeneous) catalysts are suggested in the literature. A literature search shows that a high temperature process using a gamma alumina oxide catalyst is [6] [7] possible. Alternatively, a low temperature liquid process using a super-acid polymer resin has been examined [8]. Other catalyst options are possible, including a gas phase dual function catalyst that combines both methanol synthesis and DME formation steps from syngas. The DME formation reaction equilibrium favors low temperature, but kinetics favor high temperature. You should explain your justification for the catalyst and conditions you choose. Include considerations for on-site catalyst regeneration or cost effective recycle, minimum catalyst inventory and if possible, innovative technologies to avoid intellectual property licensing costs in the design.

The produced DME must meet the ISO DME Fuel Plant Gate Standard (ASTM D7901.144734). Lubrication additives for DME are required. The exact requirements are unclear at this time, but somewhere

around 900 ppm (mass) can be assumed [5]. A bulk cost of \$1.65/lb, plus shipping (same as methanol shipping costs), for the lubricant can be used. The process must have as small a carbon footprint as possible. Please make recommendations on how this can be achieved.

Please specify any waste products generated from this facility and provide recommendations to monetize all waste products. For the purposes of your economic analysis assume the system will have a 20-year plant life, and a Minimum Acceptable Rate of Return (discount rate) of 8%. Safety and Environmental aspects should be considered in decisions and recommendations and clearly described in the report.

In the event that you conclude that DME is not economically competitive with current diesel fuel in the U.S. (on an effective \$/mile basis, ignoring the cost of conversion of diesel engines/fuel systems to DME), determine what level of government support would be required to achieve the required 8% IRR on the investment.

References:

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4. Astaxanthin Manufacture via Fermentation (Recommended by Rick Bockrath, Consultant – formerly DuPont)

Background

You are the manager of the Strategic Planning group for a major fermentation-based company. Your group has two key business roles. First, your group scouts for potential new products to manufacture; and, second, you evaluate these leads via techno-economic analysis and present the results to upper management for their consideration. Since your company is already a major player in the animal feed, human food and nutraceutical industries, your focus is primarily on those marketspaces.

One product line that you have followed for a number of years has been astaxanthin. Up until very recently the fermentation literature has shown disappointing fermentation productivity. A recent summary review article by C. Zhang (1) showed results from his laboratory with significantly higher production rates and loading in the microbial cells. The best performance was with E coli which your company understands extremely well since many of your other product lines are based on E coli. The improvement given in the article is significant enough to justify further analysis by your group. If the analysis is positive; then, management will likely want to approach the owner of the technology to discuss a commercialization partnership. You will need to make many assumptions in the course of completing the analysis and so management will expect a strongly positive result before proceeding further due to the uncertainties inherent in your analysis. An IRR of greater 25% should be sufficient. You expect that you will exceed 25% but if your analysis falls short then upper management wants to know the required price to reach 25%

Carotenoids are a family of natural red, orange or yellow pigments which are widely distributed in nature. They basically give “color” to nature. There are more than 1,000+ members of this family, but the key commercialized compounds are astaxanthin, beta-carotene, lycopene and zeaxanthin. Total revenue in 2017 was \$1.5 billion/yr. 55% of this total revenue was from astaxanthin. Growth is between 4 and 5%/yr. 75% of current manufacture is via classical chemical synthesis routes and 25% is via natural routes. You believe that with the trend toward natural product offerings, there is significant potential for your company to enter the astaxanthin business assuming adequate economics by displacing the chemical synthesis producers. The end-uses for astaxanthin are animal feed, food and increasingly nutraceuticals. You already have a very strong presence in these markets which will aid in early product placement. Recent marketing studies, which you have purchased, indicate that natural astaxanthin sells for approximately \$4,000/kg. This is a 50% higher price than chemically synthesized material. The total market is 275 tons/yr.

Project Focus

Your team has decided to focus on capturing 20% of the current market or 55 tons/yr at an average price of \$3,500/kg.

Product Form

Natural astaxanthin is sold in two forms – an oleoresin oil of 1 to 5% concentration and an oleoresin powder of 10 to 20% astaxanthin. The remainder is apparently cell debris from the recovery process. You will focus on the solid form which is believed to command a higher price. Assume an astaxanthin concentration of 20% in the solid.

Fermentation Considerations

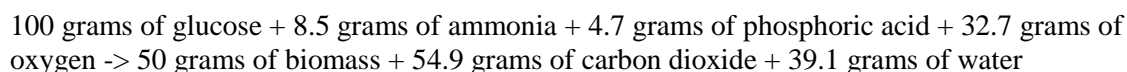
You will base your work on a recent article from C. Zhang (2) which provides some fermentation process details. Of key interest is that his lab has claimed that the product produced is the desired 3 S,3” S-astaxanthin enantiomer versus the synthetic route material which comprises a mixture of three isomers. It is clear that the laboratory work is in its very early stages and so your team has decided to undertake the technoeconomic analysis with improved “goal” metrics. The improvements, assumed over current

literature values, are based on your company's previous experience in scaling-up technology and in-depth knowledge of E coli fermentations.

a) Pathways

Figure 7 of Zhang indicates that the fermentation is basically a two-step process. Little astaxanthin is produced during active growth of the microbe. It is common in a fermentation that once a nutrient other than the carbon source is depleted, usually the nitrogen source, the cell metabolism changes from microbe growth to producing the desired product.

You retain an outside microbial consultant to support your work and she has suggested using the following equation for the growth phase:



Further she has suggested we assume a 50% carbon utilization rate during the astaxanthin production phase. She has given the team the following suggested molar material balance.



b) Microbe

The organism is a genetically engineered microbe. Physical containment and control technology must at a minimum comply with The Toxic Substances Control Act (TSCA) Part 725.422. Facilities must be designed to physically contain the live organism. It is unlikely that the highly engineered organism could survive in the wild. Nonetheless, prior to removal from the processing area, the organism must be deactivated or killed and then properly disposed of. Landfill, after astaxanthin recovery, is adequate for final disposal. Likewise, operating vents and spills that could contain live organism are to be contained and treated. The operating vent could be treated with a scrubber using a low concentration of bleach. Spills could be sent to a tank and heated to sterilization temperature prior to discharge.

c) Fermentation Design

The article by C. Zhang made use of simultaneous fermentation and extraction (SFE) to maximize astaxanthin recovery. Isopropyl myristate (IPM) was used as the extracting solvent. The IPM recovered the material that was excreted into the broth. This represents only 2% of total potential yield. Your company's experience with SFE has been quite negative due to the inability to get clean phase separations and other significant operational difficulties. For this analysis, you will assume that SFE is not practiced and the material in the broth is lost to the waste treatment plant.

Between fermentation batches, the fermenter is cleaned and sterilized to begin another batch. Your design may include multiple fermenters. You also need to provide facilities to grow the organism beginning each batch with a 1 mL vial in the lab containing 10 mg of live organism. Typically, multiple seed vials will be added to multiple 2 liter shaker flasks to begin the growth phase. The contents of the shaker flasks will be transferred into a seed fermenter (usually 1/10 the size of the production fermenter) for further growth. The contents of the seed fermenter are transferred to the production fermenter for

Metric	Literature Value	Value to Use in Study
Dry Cell Weight (grams/liter)	21	30
Product accumulation in cell (%)	1.5	2.5
Product accumulation in broth (mg/liter)	15	15
Final Titer (grams/liter of broth)	0.32	0.75
Specific Productivity (mg Asta/gram DCW/hr)	0.95	0.95
Length of Production Phase (hours)	16	26.5

final growth and production of astaxanthin. Depending on the growth rate of the microbe and the size of the production fermenters, there may also be a pre-seed fermenter (usually 1/10 the size of the seed fermenter).

Sterility in the fermentation area will be a significant concern. Suitable measures must be taken to ensure that no adventitious organisms enter the process. This would introduce competition to your proprietary microbe, which would consume feedstock and generate undesired by-products. Everything entering the fermenter must be sterile, except of course for the inoculum.

A common characteristic of all nutraceutical ingredients manufacture is that the products must be made to a high degree of purity and under very high sanitary conditions. Production equipment must be dedicated to nutraceutical ingredients and cannot be used for other industrial production. Plants producing nutraceuticals are subject to periodic inspection by the FDA.

Downstream Processing Considerations

The literature suggests that the typical downstream sequence of unit operations is:

a) Concentration of the solids (still intact)

There are two common methods to concentrate the dry cell weight in the broth to 20 wt% - disc stack centrifuges and microfiltration. Your firm's best experiences have been with disc stack centrifuges and they are recommended for this step.

b) Cell disruption

Most of the literature is focused on yeast or algae as the astaxanthin source. These are hard walled cell entities and require strong cell disruption unit operations like acid treatment. E coli has a much weaker wall and should be much more easily disrupted. Since, the product is so valuable; you want to make sure that there is complete disruption of the cell wall so that the extractant solvent can fully access the astaxanthin. Therefore, assume a homogenization step which is discussed in a number of the references.

c) Drying

The literature discusses spray drying and drum dryers. Your firm has positive experience with both technologies.

d) Dry Cell Particle formation for Extraction

The dry cell material coming from a drum dryer or spray drying will be a fluffy material that will not be in a form for use in an extractor. Some form of pelletization or other particle formation unit operation will be needed. An inert binder may be required for this step.

e) Extraction

Most of the literature seems focused on either super critical extraction or simple solvent extraction. The weight ratio of solvent used to product obtained is a key determinant of extraction technology choice. While your firm understands fermentation in great detail and many of the classic fermentation broth downstream processing technologies; extraction is one area where you will need to do further work in solvent choice and extractor design.

f) Final product recovery.

Final recovery of the solid product from the extractant. Since the marketplaces include human food and nutraceuticals, residual solvent levels must be no more than 1 PPM.

Your team has found the following articles (3 through 6) on astaxanthin downstream processing after a quick search. More research will be needed by your team before making the final choices on the unit operations to use.

General Considerations

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.

Cost structure for Carotenoids

While your company knows the animal feed, human food and nutraceutical markets, astaxanthin may be an uncommon product for your firm due to its very high price and quite small volume. One market study proposed the following cost structure for this marketplace.



<https://www.marketsandmarkets.com/Market-Reports/carotenoid-market-158421566.html>

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5. Batch Production of a Potent Small Molecule Active Pharmaceutical Ingredient (Recommended by Alex Marchut, Janssen Biopharmaceuticals Division of Johnson & Johnson)

Background

This project has been formulated to provide a pharmaceutical design project experience, using actual kinetic data for the chemical reactions and other data to produce a competitive pharmaceutical product - without identifying the Active Pharmaceutical Ingredient (API), hypothetically named Halfaxia. This problem statement identifies the principal design steps. Data will be provided for design of the process.

Most small molecule APIs are chemically synthesized in large batches, on the order of 100 kg. The Critical Quality Attributes, CQAs, are typically the chemical purity of the API and its physical properties such as solid form and particle size. A process to make the API could be as simple as a homogeneous liquid reaction followed by direct crystallization or as complex as a heterogeneous reaction sensitive to oxygen or water followed by an extraction, distillation, and finally crystallization. In both cases, filtration and drying are also used and, depending on the crystallization process and particle size requirements, sometimes a final milling step is added.

New small molecule API manufacturing facilities must be constructed so that they are flexible enough to handle both the simple and complex processes as well as anything in between. In addition, many APIs present hazards to human health in the case of occupational exposure to large quantities, so API facilities must be designed so that the equipment operators are protected from exposure to the API and manual handling of the API is kept to a minimum. Lastly, modern facilities are typically built with a good deal of automation so that paper batch records are not required, and data is automatically gathered electronically.

Project Statement

You will be working on a project where you must design a process to synthesize Halfaxia, a new potent anti-cancer API and design the production facility in which it will be manufactured. In particular, the solvent that the reaction takes place in is known (it is THF) and cannot be changed, and the solvent that the crystallization takes place in is also known (it is denatured ethanol) and cannot be changed. Other than that, you are free to design all the processing steps and conditions (for example you should optimize the reaction temperature to fully react as much starting material to product as possible, based on the kinetics that you will be given).

Once you have designed the process, you will need to design the manufacturing facility, keeping in mind all the constraints mentioned in the background. One important thing to consider is this API is not a controlled substance and the company does not foresee needing to produce controlled substances in the future, so you will not need to consider these issues in your design of the facility.

Lastly, the solvents that you will be working with in the process are flammable, hazardous, potentially corrosive to some materials, and have the potential to be volatile organic pollutants to the atmosphere. You will need to design a facility that is safe enough to handle these and minimize their release into the atmosphere.

As you design the facility, you should do your best to keep capital costs of the equipment and operating costs of the facility to a minimum. The costs of the raw materials and product are confidential, but it will be important for you to calculate and minimize the costs of both the capital investment and the daily operation of the facility.

You can build the plant anywhere in the world, but you should consider things like cost of labor and availability of dependable supplies of utilities such as electricity and water when you choose the location.

For purposes of your design, you will be given an approximate raw material starting cost and an approximate selling price of the API in its dried but unformulated state. From these prices and your capital and operating cost estimates for this part of the manufacturing process, you should seek to optimize the NPV of the process, assuming your company needs to earn at least a 20% IRR on the investment. Although estimated to be in the billions of dollars, you do not need to include the initial cost of clinical trials and FDA registration in your economics, as it is included in the economics for the final formulated product, which are confidential.

6. Enzyme Production Using Extremophilic Biocatalyst (recommended by Jeffrey D. Cohen, Janssen Biopharmaceuticals Division of Johnson & Johnson)

Recent investigations have demonstrated that extremophilic archaea, bacteria, and fungi have colonized environments that were believed to be inhospitable for survival. Cellular components of thermophilic organisms, e.g. enzymes, proteins and nucleic acids, are also thermostable. Apart from high temperature, they are also known to withstand denaturants of extremely acidic and alkaline conditions. The thermostable, halostable enzymes are highly specific and thus have considerable potential for conversions under conditions that are appropriate for industrial applications. The conditions required by these thermostable enzymes which bring about specific reactions, not possible by chemical catalysts, are still mild and environmentally benign, as compared to the temperatures, pH, and/or pressures required for many chemical conversions. The enzymes can be produced from the extremophiles through either optimized fermentation of the microorganisms or cloning of fast-growing mesophiles by recombinant DNA technology.

The biocatalyst used in this process is a genetically-modified alkaliphile, *Natronomonas pharaonis*. This genetically-modified strain was selected after adaptation to adjustments in temperature, pH, and media osmolality. The specific enzyme product of interest is a protease, having a molecular weight of about 30kDaltons, with demonstrated, optimal activity at 60°C and pH 10.0. The performance of this extremozyme at these conditions, in comparison to the leading incumbent when used at equivalent concentration, enables a price premium. The protease is formulated for use in the soap and detergents industry.

Because of the unconventional environmental conditions needed for the cultivation of extremophiles, contamination problems are minimal. Therefore, batch bioreaction, continuous-culture, or sequential partial-harvest and refill production may be used.

During accumulation in the bioreactor, the enzyme is produced and largely-retained intracellularly; however, the final enzyme product must be liberated from the cell interior and subsequently concentrated.

The objective of this project is to determine the investment, cost of manufacture, and profitability by specifying the details of:

- the upstream, process equipment capable of growing biocatalyst that produce the desired enzyme
- the sterilization equipment, needed to return supernatant liquid to the process, contamination free
- the method of releasing the enzyme from the biocatalyst
- the separation equipment capable of isolating a concentrate of enzyme from the supernatant liquid
- the downstream process equipment capable of drying the enzyme
 - drying the enzyme is an option depending on the protease application and anticipated shelf life
- the packaging equipment capable of containing the enzyme in preparation for transport and storage.
- estimating the cost and investment of biological and analytical laboratory support
- estimating the cost of utilities
- the required reagents for cell growth, pH control, foam control, and cleaning equipment.

Partial list of process and product details:

- annual production rate: 4,500 metric tons
- peak product titer: 55 grams/Liter
- cell doubling time at maximum growth rate: 1.5 hour
- peak cell density in bioreactor, bone dry basis: 35 grams/Liter
- peak oxygen uptake rate: 250mMol O₂/Liter/hour
- enthalpy of fermentation: 14,400 KJoules/Kg O₂ consumed
- bioreactor campaign production period in batch followed by continuous operation: ≤ 8 days
- dried biomass, packaged bulk density: 0.7 grams/Liter
- percentage of process uptime: 95%
- estimated price premium versus leading incumbent: 15%

Background information regarding upstream and downstream, enzyme production is contained in the listed references.

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7. Design of CAR-T Cell Manufacturing Process (recommended by Jeffrey D. Cohen, Janssen Biopharmaceuticals Division of Johnson & Johnson)

T-Cells are normal cells of the immune system that help to fight infection. T-Cells can react and kill cancer cells in the right circumstances; however, some cancers can evade the immune system. Chimeric antigen receptor T-cell, i.e. CAR-T cell treatment, involves taking some of the patient's own T-Cells and modifying them in a laboratory so they can recognize and react against their cancer. The patient undergoes apheresis, which is the process of removing some of the T-Cells, after which the T-Cells are modified in a laboratory to express receptors to better-recognize cancer. T-Cells are then expanded, i.e. grown to large numbers, concentrated, and infused back into the patient intravenously. The T-Cells that are generated all have a receptor which recognizes cancer cells, thus fortifying the patient's immune system to improve chances of recovery [1].

Most clinical trials for CAR T-cell therapies have been in hematological malignancies primarily because these cancers are easily accessible and their cell surface tumor antigens well characterized. There are specific challenges associated with the development of CAR T-cell therapies in solid tumors that are not present in hematological malignancies, including tumor size and microenvironment. Solid tumor masses contain billions of cancer cells and these cells are much harder for T-cells to access compared to individual cancer cells that are floating in the bloodstream.

Clinical trials have revealed several key challenges that must be overcome, including identifying optimal T-cell dosage and managing toxicities. Reprogrammed T-cells proliferate rapidly once they are infused back into the patient. It is important to determine how many infused T-cells are needed to elicit a safe and strong response in patients. Hematologic malignancies may behave differently than solid tumors where the T-cells need to get into the tissue and find the tumor and antigen in order to elicit a response.

Presently, patient-specific T-cells are required as the starting material. As CAR-T therapy is customized for each individual patient, the manufacturing process must be "numbered-up" versus a classic chemical engineering scale-up.

Apheresis is a procedure in which blood is withdrawn from a donor, a portion - such as plasma, leukocytes, or platelets - is separated and retained, and the remainder is retransfused into the donor. Types include plasma exchange, i.e. plasmapheresis; removal of white blood cells, i.e. leukapheresis; removal of platelets, i.e. thrombopheresis; and removal of red blood cells, i.e. erythrocytapheresis.

There can be severe 'fresh product' scheduling constraints when trying to collect enough blood from patients who are very ill because apheresis should only be collected when the patient is not experiencing any severe symptoms. Additionally, it is very challenging to isolate T-cells from a blood sample that is full of cancer cells.

Following apheresis, elutriation is used to further fractionate red blood cells from white blood cells. Elutriation is a process for separating particles based on their size, shape and density, using a stream of gas or liquid flowing in a direction usually opposite to the direction of sedimentation.

An objective of this project is to design a CAR-T production process aimed at treatment for a hematologic malignancy, e.g. Diffuse Large B-Cell Lymphoma. A further objective is to propose a method of withdrawing whole blood from a patient donor, retain the fraction of the blood used for the subsequent CAR-T production and return the remainder to the donor.

Assumptions:

- the cost of \$2.58 billion to bring an FDA-approved medicine to market

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8. Green Production of CO from Waste CO₂ Gas (recommended by Vignesh Bhethanabotla and Mavis Athene U Chen, UPenn)

The use of conventional liquid fuels has been and continues to be an integral part of the current energy sector. Hydrocarbon fuels continue to dominate due to existing infrastructure and the ease of production and consumption. However, as a result of climate change, reduction of fossil fuel resources, pricing volatility, and desire for energy independence, significant effort has been made to develop technologies that improve energy efficiency, reduce emissions of greenhouse gases, and produce fuel from renewable sources. While renewable energy production has made significant progress, with improvements to technologies such as solar panels, etc., energy storage remains a challenge. In the transportation sector, which demands portable energy storage, gasoline boasts an energy density of 47.5 MJ/kg, while the lithium ion batteries used in current battery electric vehicles (BEVs) compares poorly at just 0.3 MJ/kg [1]. Development and production of sustainable and renewable materials with equivalent functionality to traditional petrochemical fuels is of high importance. Battery technology still lags behind gasoline in energy and power density. Other chemical fuels, such as hydrogen gas, lack the existing infrastructure that traditional hydrocarbon fuels benefit from. Production of hydrocarbon fuels from a renewable source, therefore, is an attractive line of effort. Bio-based production methods are limited by the risk of competing with food production for agricultural resources, and so direct conversion of atmospheric or point-source pollution CO₂ serves as an exciting possibility.

The Fischer-Tropsch process provides a means of production of liquid hydrocarbon fuels but requires CO and H₂ inputs [2, 3]. Reduction of CO₂ provides a source of CO while simultaneously mitigating the effect of a prevalent greenhouse gas. A new technology developed by Haldor-Topsoe provides a possible avenue to this end. The eCOs technology and process is advertised to produce CO from CO₂ using a solid oxide fuel cell (SOFC) through electrolysis [4]. The eCOs technology is advertised as producing CO with over 99.0 vol% purity with 6 kWh per Nm³ of CO produced. Active materials for heterogeneous CO₂ reduction may also be worth consideration and comparison [5, 6].

The overall process is envisioned in several steps. First, CO₂ must be sourced from capture or extraction for a feed stream. The most desirable source of CO₂ is from the atmosphere or from point sources where it is produced as waste in order to further an environmental and sustainability-focused goal. Then, utilizing the proposed SOFC technology, or a similar technology, the CO₂ to CO conversion process will be designed. Ideally, carbon neutrality is possible with this technology but will depend on the energy source. Renewable sources of energy, such as solar power, could aid in achieving carbon neutrality. Finally, the economics of the overall production of carbon monoxide should be considered. The minimum acceptable price for the CO output as a function of carbon tax and other incentives, and as a function of the rate of return (IRR) required on the investment should be determined, and the demand for such a product should be assessed relative to its use in the production of liquid hydrocarbon fuel or other products that utilize CO input.

The overall process will be designed with a target of 2000 barrels/day (bbl/day) of liquid hydrocarbon production (approximately 318 m³/day). While small compared to the typical capacity of oil refineries, this target will provide a starting point for this new technology. With this end target in mind, back calculating the amount of CO required using a Fischer-Tropsch yield of 60 percent gives an approximate target of 5x10⁵ kg/day of CO production. For the sake of a round number, the target can be approximated to 250 SCMM.

The goal of this project is to develop a commercial plant utilizing this SOFC technology and determine its commercial viability. Considerations of facility location, fuel products, regulatory requirements, and carbon taxes and credits will be necessary in determining the extent of commercial viability. Additional considerations of sensitivity to raw material pricing, product mix as a function of changing demand, and equipment pricing will need to be taken as well.

In addition to commercial viability, this project aims to produce a design that is as environmentally friendly as possible. At a minimum, federal emission regulations should be met, while the goal is to strive for carbon neutrality. Safety and controllability of the plant is also a priority.

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9. Producing High Grade Hydrocarbon Fuels Through Green Processes Sourced from Waste Produced Carbon Monoxide (recommended by James Kwon and Dakota Wallach, UPenn)

Hydrocarbon gas liquids (e.g gasoline) are a necessary component of modern society as evidenced by the consumption of approximately 2.6 million barrels per day in the US.¹ Despite the myriad of proven negatives that are inherent to its use such as emission of greenhouse gases and the limited hydrocarbon resources that exist on Earth, the lack of cleaner, economically viable alternatives suggest that these fuels will continue to dominate. As such, there are no shortage of initiatives to research and develop new processes to lessen our dependence on hydrocarbons as a source of energy. By developing new methods of production for hydrocarbons that are synthesized renewably, the environmental burden of fuel production is lessened, paving the way for a more sustainable future.

One potential solution to this problem is the utilization of a novel method for the synthesis of high-grade hydrocarbon fuels, using the well understood Fischer-Tropsch (FT) process with renewable sources for the required carbon monoxide (sourced from previous CO₂ to CO project) and hydrogen inputs. The hydrogen that would be utilized in this process could be obtained from two main renewable sources. The first source is electrolysis of water, which produces hydrogen gas and oxygen with water and energy as the only inputs, utilizing novel catalysis techniques to alleviate the heavy electricity requirements of such a process.

Additionally, one can consider obtaining hydrogen in the form of coke oven gas (COG), which is a waste product of many other industrial processes. However, many countries do not make use of this waste, as China produces 70 billion N m³ annually and yet only uses approximately 20% of the gas as fuel.² Utilization of this COG, which is mainly hydrogen gas and methane, would not only be a potential source of hydrogen for this process, but also help to remove this pollutant from the atmosphere, creating a win-win scenario. The output of the FT process is high-grade hydrocarbon fuel, meaning that desirable commercial products can be obtained without further environmental pollution.

Your team is tasked to design a commercial scale plant and present economic estimates for a facility that is able to take an input of carbon monoxide (purchased from the previous group at a fixed, agreed upon, price) and hydrogen gas, sourced from electrolysis (or possibly through the refinement of COG) and produce hydrocarbon fuels as a product. The overall process will be designed with a target of 2000 barrels/day (bbl/day) of liquid hydrocarbon production (approximately 318 m³/day). While small compared to the typical capacity of oil refineries, this target will provide a starting point for this new technology. Determine the profitability (NPV) of this process as a function of carbon taxes or other incentives, based on the agreed-upon price of CO and market prices for other raw materials and products.

The location of this facility should be part of your economic consideration as countries such as China, India, U.S, and Australia continue to be the biggest users of coal, showing that demand for such hydrocarbon fuels is still immensely high.³ The plant should be designed with the goal of being as environmentally friendly as possible and at minimum carbon neutral.

References

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10. Methionine Production (Recommended by Stephen M. Tieri, DuPont)

Methionine is an essential amino acid for humans and animal growth. Since it is not naturally synthesized by humans or animals, it must be obtained from their diets, either directly or through methionine-containing proteins. While methionine has applications in both pharmaceuticals and cosmetics, 98% of global methionine production is used as an animal feed additive, most significantly for poultry and swine. As a feed additive, it contributes to the efficient, healthy and environmentally friendly nutrition of livestock, which makes it an important component of ensuring a sustainable animal protein supply for the world's growing population. Traditional synthetic methionine is commercially available in two varieties: D,L-methionine (DLM), a racemic mixture of the two stereoisomers, and methionine hydroxy analog (MHA). For animal nutrition, the two are equivalent. Although methionine is mainly derived from petrochemical sources, biochemical routes have been developed.

Your company maintains a significant presence in the global methionine market, and through its internal research and technology development efforts and acquisitions, the company has built and maintains a portfolio of technology and process options for both DLM and MHA production. In recent years, it has strengthened this portfolio with the addition of fermentation process technology. Given the continued growth in the global methionine market, and having evaluated potential retrofit options for existing facilities, the company is interested in further expanding its production capability with a new world scale production facility. While company executives and business management are eager to commercialize the new fermentation technology, they recognize that selecting the specific product form and technology with the strongest overall economic potential is critical for maintaining market share, pricing margins, and their position in this globally competitive commodity market.

Your project team has been assembled to identify the optimal methionine product form (DLM or MHA), process technology, and to design the new methionine plant to produce 150 ktonnes/yr (kilo-tonnes, thousand metric tons per year). The team is also responsible for identifying and minimizing the required investment, operating costs, and for identifying any critical economic sensitivities to raw materials, utility consumption, equipment cost, or product pricing. While the final facility location has not yet been determined, company management has narrowed the potential choices to the US Gulf coast, the US Midwest (Iowa, Nebraska, etc.), and Singapore. Your team is responsible for identifying the preferred location, and identifying the investment and manufacturing cost differences associated with the alternate location options. Current market pricing is to be expected for all raw materials, utilities, and product, regardless of location. The business and supply chain teams suggest that using corn syrup (or HFCS) feed is likely to be economically advantageous for the new fermentation process.

The plant design should be as environmentally friendly as possible, and as necessary as required by state and federal emissions legislation. It is expected that the facility will include emission control equipment as a part of the process design and operation. 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. As the process technology integration and design team, you will be there for the start-up and will have to live with whatever design decisions you have made.

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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11. Mixed Plastics Waste to Ethylene and Propylene Feedstocks (Recommended by Stephen M. Tieri, DuPont)

Plastics and polymers are integral to the modern world and global economy, enabling innovations in transportation and construction efficiency, personal and food safety, electronics, and communication. The inherent durability and potential to adjust physical and mechanical properties with recipe adjustments provides for a fabulous range of applications, but adds significant difficulty and complexity to the question of how to handle the material once the products have satisfied their intended purpose. Traditional plastic/polymer recycling technologies are largely optimized for “clean” uncontaminated material scrap from primary manufacturing consumer goods and packaging. The unfortunate end-of-life destination for many post-consumer-use plastics is at best a landfill, or incineration for the heating value, and at worst it is our rivers and oceans. Addressing global plastic waste issues to reverse existing climate change, ecosystem, health, and economic impacts (and minimize additional ones) creates new opportunities for innovation and scientific development.

Plastic Energy, LLC has developed technology to convert mixed, contaminated, multi-layered, and no-longer mechanically recyclable plastics to create virgin-quality plastic process monomers. This technology provides an opportunity to more directly recycle and re-use a polymer’s carbon content; avoiding the material, energy, costs and environmental risks associated with extracting additional petroleum (including exploration, drilling, pumping, transportation, etc.). At a high level, the process utilizes household and industrial plastic waste (polypropylene, polystyrene, and high- and low-density polyethylene) to produce monomers of equivalent composition and quality to industry standards from typical petroleum feeds. More specifically, the technology uses thermal anaerobic conversion, high temperature, and oxygen-free conditions, to produce hydrocarbon vapors. After the non-condensable pyrolysis product gases are separated (with potential combustion for process energy), the condensable gases are fed to distillation columns where naphtha is separated out for re-use in the production of monomers or as fuels. The technology as currently practiced is robust and accepts all classes of plastics; however, resin identification codes (recycling types) 2, 4, 5 and 6 are preferable.

From a chemical process standpoint, the Plastic Energy technology focuses on transforming end-of-life plastic waste destined for landfill, incineration, or the ocean into a range of oil products which can be used either as a feed to generate clean recycled plastics and contribute to a circular carbon economy (Plastic2Plastic) or as an alternative fuel with a low-carbon footprint (Plastic2Oil). In addition to their pilot and process development facilities in London, Plastic Energy has commercial operating facilities in Spain. While the two Spanish sites currently produce fuel products, the additional process steps necessary for product oil conversion to circular economy monomer feeds are accomplished using industry standard technology and equipment.

Your company is currently perceived as traditional linear economy type carbon consumer/user (mine raw materials to product products which are thrown away after use), and is working to transform its image into one that recognizes current environmental and climate change challenges and takes an active role as global leader in initiating and driving a circular carbon economy solution. To this end, your company is working to negotiate a partnership agreement with a Plastic Energy for use of their technology to produce the “circular” polymers for the global market. Although many of the agreement details are not yet finalized, with its market position, experience, and resources, your company will design, construct and operate the first-generation commercial scale Waste Plastic-to-Monomer facilities. It is expected that successful startup and operation of the first facility will be followed by strategic investments to provide global production capability for circular plastics.

Compared to other recycling technology options, the company technology leadership is excited by the inherent process flexibility of the Plastics Energy technology to minimize the need for feed plastic washing and sorting. Specifically, they see an opportunity to avoid investment and cost associated with

the additional processing steps/unit operations in addition to the increased water use, waste material handling, energy, and operation uptime issues associated with “dirty” plastic waste. While company executives and business management are eager to commercialize the new waste-to-plastics technology, they recognize that selecting both the specific circular ethylene and propylene product mix and the facility location with the strongest overall economic potential is critical for establishing market share, pricing margins, and their position in what is expected to quickly become a globally competitive commodity market for circular economy monomers. Following lengthy internal polymer capacity evaluations, supply chain reviews, and logistics assessments; company management identified the Netherlands, Indonesia, and California as potential location options for the new facility.

Your team has been assembled to provide an independent evaluation of the Plastic Energy technology as an integrated part of a new ethylene/propylene monomer facility, and estimates of the potential investment and expected operating costs. The investment and manufacturing cost estimates are key to validating the initial economic profit estimates and as input into final negotiations with Plastic Energy. The project’s business objective is to design a commercial scale facility to convert 70 MT/day (dry basis) mixed plastic waste to produce ethylene and propylene. The waste plastic feed is expected to be a typical blend of post-consumer, post-industrial rigid, and film type 2, 4, 5, and 6 plastics. The waste plastic feed is also expected to be both wet and “dirty”; with moisture, oils, organic/food residue, and with pigment solids (TiO₂ and other pigments). Since one of your company’s stated sustainability goals is to produce circular polyethylene (PE) and polypropylene (PP), certified to International Sustainability and Carbon Certification plus (ISCC+) circular content standards; the ethylene and propylene monomers will need to meet to enable the ISCC+ certified PE and PP products. Any diesel fuel co-product will need to comply with ASTM D975 and EN590 standards. Current market pricing is to be expected for products (ex. ethylene and propylene), raw materials (including mixed plastic waste), and utilities.

Your team is responsible for identifying and minimizing the required investment, operating costs, optimal product mix, and identifying any critical economic sensitivities to raw materials, product mix, utility consumption, equipment pricing, or product/co-product pricing. While polyethylene and polypropylene polymer production capacity, potential expansion requirements, and/or additional supporting monomer storage facilities are outside the scope of this project, the design and investment estimates should include appropriate circular monomer product storage capacity to reasonably segregate product material for quality testing and decouple the new independent monomer process from the existing PE and PP polymer processes.

The plant design should be as environmentally friendly as possible, and as necessary as required by local, state and federal emissions legislation. It is expected that the facility will include emission control equipment as a part of the identified process design and operation. Recover and recycle process materials to the maximum economic extent reasonable. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate. As the process technology evaluation, integration and design team, you will be there for the start-up and will have to live with whatever design decisions you have made.

You will need additional data beyond what is provide above and listed in the references below. Cite any literature data used. If required, make reasonable assumptions, state them, and identify to what extent your design or economics are sensitive to the assumptions you have made.

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12. Conversion of Graphite to Graphene Derivatives by Oxidative Digestion (Recommended by Dr. Matthew Targett, SpruceWorks LLC)

Overview

Graphene is a two-dimensional monolayer of carbon atoms that has outstanding mechanical, chemical and electrical properties. Physicists Konstantin Novosolev and Andre Geim, first discovered graphene in 2004^{1,2} using a mechanical exfoliation method now known as the “Scotch Tape method” to form small flakes of graphene with a thickness of several microns. In 2010, they were awarded the Nobel Prize for their discovery.

Graphene holds promise as a “wonder material” exhibiting a number of record-breaking performance characteristics. Graphene is currently the strongest material with the lowest density, with strength ~200 times that of steel. Graphene is highly stable and highly elastic, and combines the hardness of diamond with the flexibility of ultra-thin films. Graphene has the potential to revolutionize microelectronics and computer technology as it also shows electrical hyperconductivity and thermal conductivity. As a lab fascination, graphene is already gaining traction in performance markets and will find its way into new applications, many of which may not be fully envisioned at present. Some applications shown in Figure 1 are being developed for this material, while large-volume production processes are still in development.

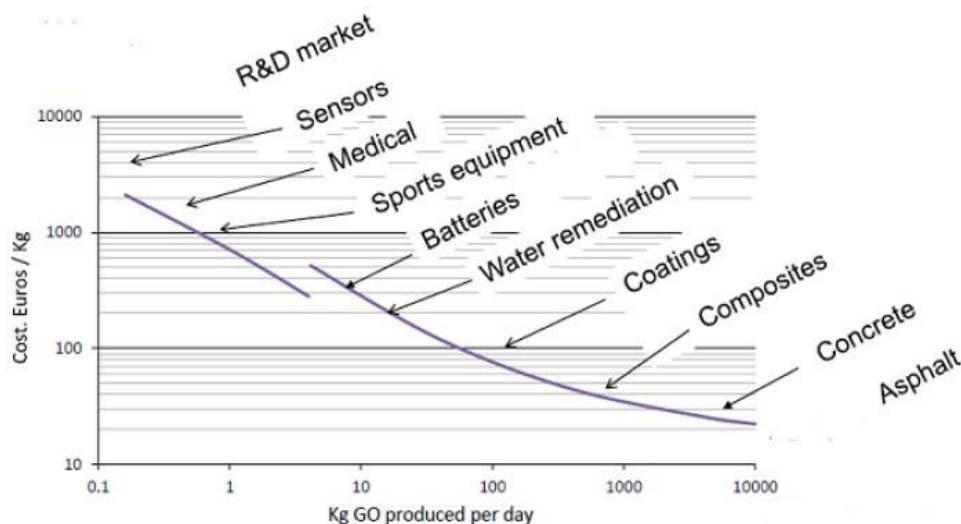


Figure 1: Graphene Oxide Markets and Acceptance Based on Price Points

Source: Abalonyx company presentation

One key challenge that is limiting graphene’s growth potential is its high production cost. Current lab batch synthesis techniques are too costly to support graphene’s full growth potential. As such, continuous

¹ Novosolev, K.S. *et al*, **Electric Field Effect in Atomically Thin Carbon Films**. *Science* 306, 666-669 (2004)

² Geim, A.K. & Novosolev, K.S. **The Rise of Graphene**. *Nat. Mater.* 6, 183-191 (2007)

industrial processing techniques are needed to reduce manufacturing costs, allowing for price reductions, and to ultimately drive high rates of market growth. This is a classic commercial scale-up challenge, very simply depicted in Figure 2.



Figure 2: Lab Scale-Up Challenges (from Nelson)

Graphene can be synthesized by two different strategies, so-called Bottom-Up and Top-Down approaches. The Bottom-Up strategy comprises those methods in which a carbonaceous gas source is used to synthesize graphene. These methods include epitaxial growth on silicon carbide and chemical vapor deposition (CVD) techniques. Some of these methods can provide large-scale graphene, but it is difficult to detach the product graphene from the substrates and the costs of the substrates can be relatively high.

In contrast the Top-Down methods are based on ‘attack’ of graphite powdered raw materials to break down its layers to form thin layers of graphene platelets. These methods include micromechanical cleavage, exfoliation of graphite intercalated compounds, solvent-based exfoliation, unzipping carbon nano-tubes, and exfoliation or reduction of graphite oxide (GrO) and its derivative graphene oxide (GO). One such sonication technique is shown in Figure 3.

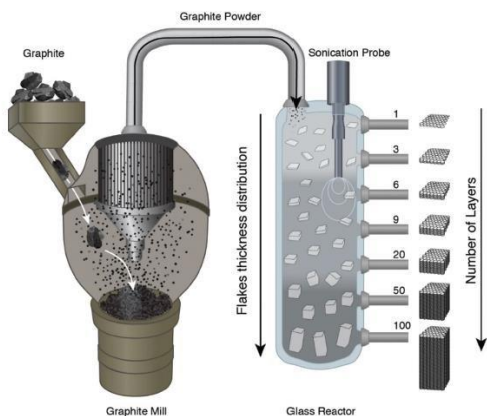


Figure 3: Liquid-Phase Exfoliation of Graphene, from Kauling et al (2018)³

For the purposes of this project, the objective will be to determine the optimal commercial oxidative digestion process configuration for converting graphite to useful graphene-derivative products, namely graphene oxide and/or graphite oxide. It is recommended to base the main conversion process directly on

³ Alan P. Kauling, Andressa T. Seefeldt, Diego P. Pisoni, Roshini C. Pradeep, Ricardo Bentini, Ricardo V. B. Oliveira, Konstantin S. Novoselov, and Antonio H. Castro Neto; **The Worldwide Graphene Flake Production**. *Advanced Materials*, 1803784 (2018)

the experimental batch data reported by researchers from the University of Castilla-La Mancha (2016)⁴ and to scale-up their small batch oxidative digestion process to a continuous process at an industrially relevant scale.

In terms of a rigorous and detailed project structure, the following approach is recommended at the outset. The key to a techno-economic evaluation success is a sufficiently accurate process simulation model covering major processing steps; namely, oxidative digestion reactor design, taking into account product yields and reaction kinetics, off-gas handling, spent acid handling and to the extent necessary an integrated heat integration process. The process simulation model should take into account user-defined Key Input Variables (KIVs) and have the ability to predict Key Output Variables (KOVs). Some of the key input variables will be fixed.

Project Statement – defined criteria

- Utilize natural graphite as feedstock
- Utilize so-called “Optimized Improved Hummers Method”⁴ as process design basis
- Capacity: 10 ton per day product output, continuous process
- Products Purity, flake size specification and Raman spectroscopic specifications to be determined as part of this project based on variability in commercially available materials⁵
- Product selling prices, use \$10/lb as initial target, but use cost-volume elasticity shown in Figure 1 as a means to determine optimum technoeconomic case

Key Input Variables – to be varied for the purposes of determining lowest Capex-Opex operation

- type of digester (temperature control, operation safety and ‘run away’ avoidance, etc.)
- off-gas utilization (determine how best to handle off-gases, recovery and remediation)
- spent acid utilization (determine how best to handle aqueous waste streams, recovery and remediation)
- residual solids utilization (determine how best to handle waste solids, recovery as co-product, and remediation)

Key Output Variables – to be determined by modelling/optimization via varying of Key Input Variables

- OPEX cost, \$ per ton of products
- Capex investment, \$ per ton of production
- IRR/NPV

Note: The author of this project is not based in Philadelphia. Many or all interactions will be through SKYPE, phone and/or email.

⁴ Maria del Prado Lavin-Lopez *et al*, **Influence of Different Improved Hummers Method Modifications on the Characteristics of Graphite Oxide in Order to Make a More Easily Scalable Method**. *Industrial and Engineering Chemistry Research*, 1283612847 (2016)

⁵ Alan P. Kauling, Andressa T. Seefeldt, Diego P. Pisoni, Roshini C. Pradeep, Ricardo Bentini, Ricardo V. B. Oliveira, Konstantin S. Novoselov, and Antonio H. Castro Neto; **The Worldwide Graphene Flake Production**. *Advanced Materials*, 1803784 (2018)

13. Process Intensification using Dividing Wall Column (Recommended by Adam A. Brostow, Honeywell-UOP)

900 MM SCFD of Y-Grade natural gas liquid (NGL) is separated into components. The feed composition in mole fractions is given in Table 1.

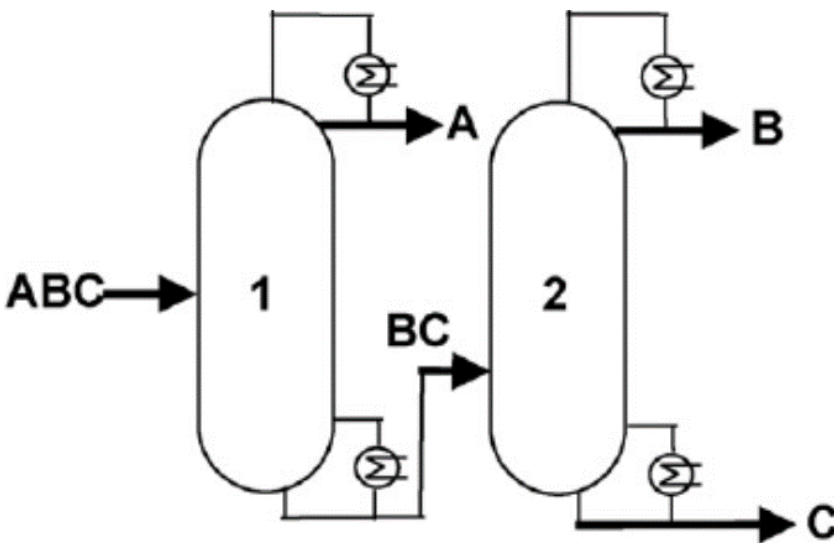
Table 1

13.04%	C2
43.48%	C3
10.87%	I4
10.87%	C4
10.87%	I5
5.43%	C5
5.43%	C6

Ethane (C2) price is low and it is to be rejected as vapor and used as fuel. The desired product is light petroleum gas (LPG), a mixture of propane (C3) n-butane (C4) and isobutane (I4), recovered as liquid. The heavier components (C5+) are also recovered as liquid.

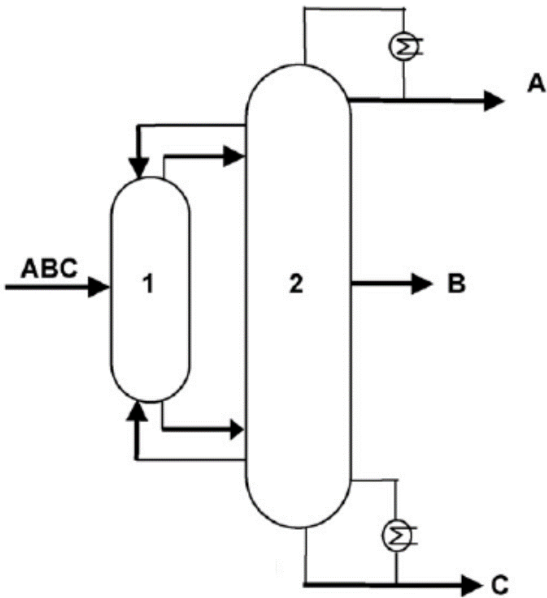
NGL is at 80 deg. F, 300 psia (conditions can be adjusted). The conventional fractionation system is a direct 2-column sequence shown on Fig. 1.

Fig. 1



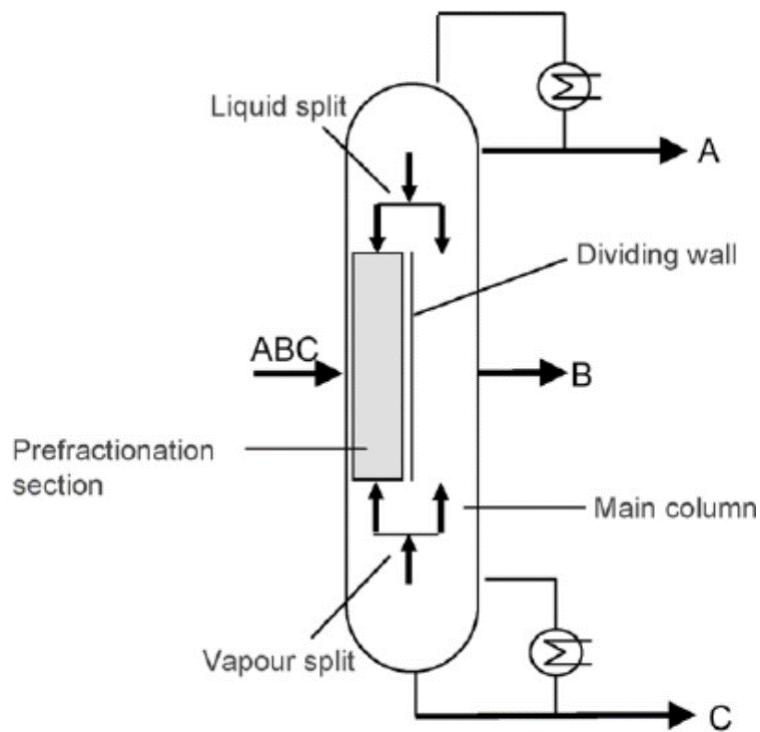
To potentially improve efficiency, one can use a fully thermally coupled configuration, so-called Petlyuk configuration, shown on Fig. 2

Fig. 2



The Petlyuk column can be configured as dividing wall column (DWC), shown on Fig. 3.

Fig. 3



Going to configuration on Fig. 2 eliminates a condenser and a reboiler. The one on Fig. 3 eliminates a column.

Problem Statement

Your mission, should you choose to accept it, is to design the DWC separating C2 from LPG and C5+ (three products).

The partial condenser with vapor products cannot be colder than -40 deg. (C or F; it's up to you to choose units). The limitation is NBP of propane used as cold utility to avoid going to vacuum at the compressor suction. Notice that Figs 1-2-3 show a generic total condenser with liquid product (A).

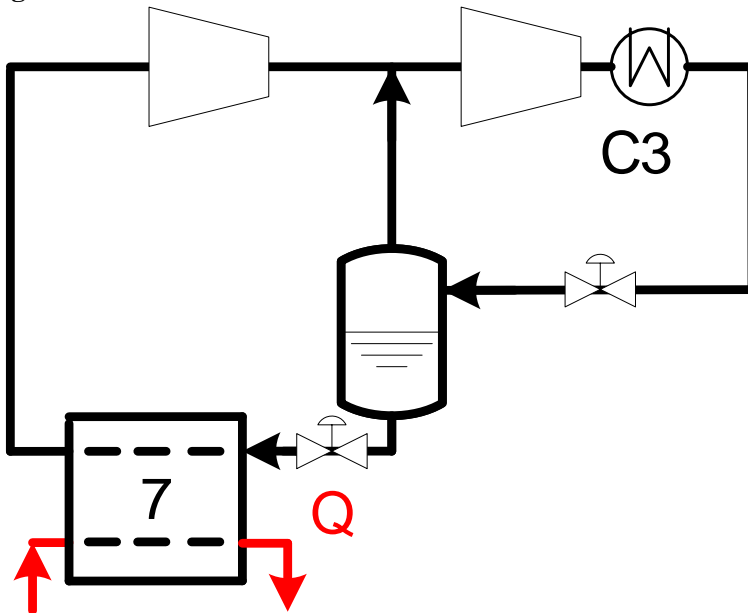
LPG recovery is to be $> 95\%$, molar basis. C2 impurity in LPG is to be $< 2\%$. C5 impurity in LPG is also to be $< 2\%$.

The cooling water utility is available at 80 deg. F. Approaches on heat exchangers are 5 deg. F. Adiabatic efficiency of compressors is 85% .

The next best alternative (NBA) to compare against is a direct sequence, as shown on Fig. 1.

Your design team will simulate the NBA and the DWC (tip: it can be simulated as two columns with two recycles, or as four columns) and compare capital expenditure (CAPEX) and operating cost (OPEX). The first step may be to size the fully thermally coupled configuration as two columns, without the dividing wall. The de-ethanizer (DEC2, first column in the direct sequence) and the DWC condensers will operate below ambient temperature (do you know why?) and will require mechanical refrigeration, part of CAPEX and OPEX. DELPG column's (2^{nd} column in direct sequence) condenser is at no less than 80 deg. F (ambient cooling).

Fig. 4



Your team is expected to simulate and optimize a 2-stage, single effect propane (C3) refrigeration system. Can one apply project intensification here?

The problem will require good understanding of distillation and significant simulation skills. The suggested steps show alternative analysis heuristic:

- 1) Simulate and cost the NBA: a direct sequence.

- 2) In the first approximation, obtain the propane chiller power from literature.
- 3) Simulate fully thermally coupled configuration. Calculate cost assuming two separate columns.
- 4) Modify cost assuming the DWC.
- 5) Rigorously model the propane chiller for both cases. This can be done earlier by a dedicated team member. Assign different roles for different team members.
- 6) Compare with the NBA to determine the improvement in NPV your design provides.
- 7) Produce pie charts of cost breakdown: CAPEX only and CAPEX plus OPEX.
- 8) Do sensitivity analysis to find best scenarios. What if we assume lower purity? What if the C2 product is produced as liquid? What if we can sell it?

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Note: The author of this project is not based in Philadelphia. Many or all interactions will be through SKYPE, phone and/or email.