

## Suggested Design Projects – 2018-2019

### 1. Green Glycol: A Novel 2-step Process (Recommended by Gary Sawyer, CDI Corporation)

Ethylene glycol (EG) is an important industrial material, with its largest use as a component (27% by weight) in a 28 million ton/yr polyethylene terephthalate (PET) market<sup>1</sup>. Conventional production of ethylene glycol uses ethylene from fossil fuels to make ethylene oxide, which is then hydrolyzed to ethylene glycol.

PET made at least partly from renewable resources has been of interest for some time. Coca-Cola introduced its fully recyclable PlantBottle® using EG from ethanol<sup>2</sup>. Using conventional, available technology, ethanol is first dehydrated to make ethylene, which is then separately oxidized to ethylene oxide.

Researchers at Leiden University have investigated catalysts that can directly produce ethylene oxide in one step from ethanol<sup>3</sup>. The ethylene oxide is then reacted with water to make ethylene glycol and higher adducts (di- and tri-ethylene glycol). Uncatalyzed reaction rates are available<sup>4</sup>.

Your project is to design a plant to produce 200,000 metric tons per year of ethylene glycol - roughly half a world-scale conventional EG plant – based on the catalysis work done at Leiden University. You will need to select from their work the conditions you conclude will give the best design. Important considerations in your design and report will include:

- A discussion of why you chose the particular catalyst and operating conditions in the Leiden work.
- The design must account for any non-selective products made from ethanol conversion, such as diethyl ether or carbon dioxide.
- The raw material is fuel grade ethanol<sup>5</sup>. Account for any impurities such as water and methanol. Consideration should be given to their removal upstream of the conversion reactor.
- The product ethylene glycol must meet Fiber Grade (a.k.a. Polyester Grade) specifications<sup>6</sup>
- The ratio of water to ethylene oxide (EO) will impact the ratio of product glycols (mono-, di-, and tri-). All are saleable, but the markets are small for the di- and tri- ethylene glycols. You must select a design ratio of water to EO and discuss why. A typical EG unit may look to market 10% of its output as di- and tri-.
- Unreacted water from the EO hydrolysis is distilled and recycled. To save energy, this can be done with multiple effect evaporators, each at a different design pressure, so that the condenser from one provides heat to the reboiler in another. You must decide on the number of evaporator stages, but typically 2 or 3 are economical.
- Determine the selling price of “green glycol” EG that provides a 15% internal rate of return (IRR) on the plant investment, based on fuel ethanol prices<sup>7</sup>.

## **References**

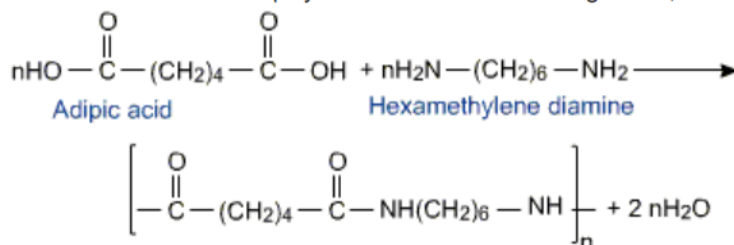
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## 2. Nylon Manufacturing Facility Design (Recommended by P. C. Gopalratnam, Consultant – formerly DuPont, INVISTA)

### 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). Reducing the pH would require 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.

It is important to not only design a process that is technically feasible but also controllable. You will need to propose control strategies for the flowsheet variables such as temperature, level, pressure and pH indicating needed measurements. Are there any special requirements for unsteady state conditions, such as start-up or shutdown? Is any additional equipment required to achieve good control, such as holdup tanks, or heat exchangers?

You must keep safety and sustainability 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? 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](https://en.wikipedia.org/wiki/Nylon_66)

### 3. Ethanol to Ethyl Acetate (Recommended by Bruce M. Vrana, DuPont and UPenn)

Ethyl acetate is used in a variety of applications, including as a solvent, because of its low toxicity. Key applications are nail polish remover, paints, adhesives, cleaning circuit boards, etc. Global sales exceed \$4 billion per year and are growing faster than global GDP. Although the ethyl part of the molecule can come from either fermentation or synthetic ethanol (making it at least sometimes “green”), the acetate part of the molecule comes almost exclusively from synthetic acetic acid, made from methanol and carbon monoxide (decidedly not “green”, given the energy intensity and acute toxicity of CO).

Greenyug, LLC, a small, privately-held startup company based in Santa Barbara, has developed and is commercializing a new process that uses (fermentation) ethanol as the sole feedstock. Although the process will be much more sustainable than conventional ethyl acetate, coming 100% from renewable resources, Greenyug also claims that it will be cost competitive with – or even more economical than – petrochemical ethyl acetate, depending on the relative price of oil and ethanol.

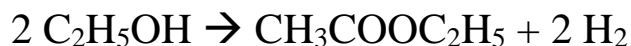
Wild claims from startup companies, especially in the biotech arena, are commonplace, and usually do not translate into commercial success. Often, they seem like a ploy to get attention (and money) from venture capital firms or existing players in the industry. As a conventional manufacturer of ethyl acetate, your company has dismissed such claims in the past. However, the fact that in 2018 Greenyug is in the midst of actually building and starting up a commercial scale facility at ADM’s corn processing plant in Columbus, NE caught your senior management off guard.

Although the ethanol feedstock comes from a fermentation plant, Greenyug is not doing any biotech. They have patent applications using heterogeneous catalysis to convert ethanol directly to ethyl acetate. Furthermore, their applications indicate they have reactive distillation technology to make ethyl acetate in a simple, low cost process. Reactive distillation has recently received attention from the AIChE as part of its RAPID process intensification effort. And Greenyug has demonstrated the technology at a pilot plant in Pune, India. Unfortunately for you, all of that makes their claims a bit more credible.

A 9/5/18 local news report of the ribbon-cutting ceremony (last reference, including video) caused your CEO to take immediate action and commission your team to rapidly put together a process design for the Greenyug plant and to estimate their capital and operating cost. The key question is what green premium – if any – Greenyug will need to get on top of the market price of ethyl acetate to achieve a 15% IRR on their investment. And how does this premium vary with the prices of ethanol and oil? Under what circumstances can they compete economically with you (putting your company and your job at risk)?

Assume that Greenyug gets the ethanol at \$0.10/gal below published (CBOT) prices for Chicago ethanol, due to logistics savings in the supply chain, being located next to a large ethanol plant. Assume that the trade journals are correct and that Greenyug (through its subsidiary Prairie Catalytic LLC) is building a 50 kt plant. Assume that ADM will supply steam and other utilities at market prices. But otherwise, Greenyug (Prairie Catalytic) will be an independent company, responsible for its own investment, maintenance, operations, technical support, etc.

The overall main chemical reaction is



This begs the question of what to do with the hydrogen coproduct. The patent applications indicate that it can be used to hydrogenate liquid coproducts such as butyraldehyde and 2-butanone (MEK). It seems likely that this will be needed to meet the typical purity spec of 99.8% min for ethyl acetate, which Greenyug must meet to sell into all markets. But there will still be an excess of hydrogen. Assume that excess

hydrogen can be used on the site complex at a value of \$1/lb (2019 dollars). If this is a crucial part of your economics, estimate a fair price to sell hydrogen to ADM as rigorously as possible and include it in your sensitivity analysis. You will also need to decide what to do with the other byproducts after they are separated from the main ethyl acetate product.

Obviously, your company – and thus your group – cannot have any contact with Greenyug at this time, since they are a potential competitor. Thus, you must base your design only on what can be gleaned from public information, such as the references and any other published information you can find. You may not contact anyone affiliated with Greenyug, including academic partners at UCSB and elsewhere.

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 in deciding whether Greenyug is a threat. 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 your management can decide on an action plan.

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. Be sure to consider how the plant will be started up in your design.

## **References**

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#### **4. Process for Sustainably Sourced 2,5 Furan Dicarboxylic Acid (Recommended by Rick Bockrath, Consultant – formerly DuPont)**

##### **Problem Statement**

You work for a major plastic manufacturer. Your company is interested in exploring the market for sustainably sourced polyesters such as PET. One part of the PET polymer is ethylene glycol. Producers in Brazil have apparently successfully started up commercial scale EG plants based on ethanol and are able to command a significant price premium over petrochemical EG (up to 100%) for select markets. Your company's interest is in understanding the other side of the polymer – the diacid. Your marketing organization is optimistic that the fibers segment can accept the needed upcharge for a 100% sustainable product.

Last year, a team was tasked by the marketing organization with exploring sustainably sourced p-xylene for use as a feedstock in p-terephthalic acid (TPA) manufacture which is the other monomer in PET plastics. It was hoped that the TPA made from sustainable p-xylene would not require a significant upcharge over current pricing and you could manufacture a straightforward “drop-in” product. Unfortunately, their study indicated that a significant increase in TPA cost would be required due to the much higher cost of sustainably based p-xylene. After in-depth discussions with key customers, the marketing organization concluded that the upcharge could not be supported by the marketplace. Further work on this approach was stopped.

The marketing organization is still very interested in a sustainable solution and has suggested that your team explore “non-drop-in” sustainable plastics. They have had further discussions with key customers who suggested using 2, 5 furan dicarboxylic acid instead of TPA for the diacid side of the polymer. Ideally the new plastic will be similar enough to PET in performance, handling and cost that it will not be disruptive to the current users' processes and still meet current customers' key needs. Marketing is optimistic since studies have found that FDCA based plastics, when compared to PET, have:

- a) Up to 10 times better O<sub>2</sub> barrier performance
- b) Up to 4 times better CO<sub>2</sub> barrier performance
- c) Up to 2 times better water barrier performance
- d) A desirable higher T<sub>g</sub> of 86 °C versus 74 °C
- e) A T<sub>m</sub> of 235 °C versus 265 °C
- f) Recyclability has been demonstrated.

Your team is tasked with developing a plant design and economic estimates for a FDCA facility making a crude product based on recent patents and other technical literature. The ultimate product is highly pure FDCA based resin for fibers. Since creating a final polymer grade monomer requires very specialized knowledge, the marketing organization has contracted with an outside consultant to develop the process and cost details for upgrading the “crude FDCA” to a final high-quality monomer. Therefore, the final purification of the “crude FDCA” is outside of your scope. The consultant has suggested for now that your team should assume that the final purification step will cost \$0.10/lb in OPEX and \$0.15/lb in CAPEX.

Your focus is on defining the magnitude of the needed premium to make the venture profitable versus TPA. Please remember that FDCA has a 6% lower molecular weight than TPA and so you will need to take this into account in pricing.

## Background

The route to FDCA is a two-step process. One starts with hexose sugars like glucose, fructose or high fructose syrup as the feedstock. The preferred sugar is fructose due to its much higher reactivity. Therefore, high fructose syrup (HFS) which is now in excess due to shifting customer tastes would make a good feedstock. Since HFS still contains glucose, a catalyst is added to the sugar to ensure the glucose is converted to fructose for conversion in the first step. The first step involves the formation of hydroxymethylfurfural (HMF) from the sugar via dehydration. The second step involves the oxidation of HMF to 2,5 FDCA. While these steps have been studied for many years, the conversions have been plagued by low yield and low selectivity. As an example, rehydration of HMF generates formic acid and levulinic acid. Polymerization of HMF and fructose leads to highly insoluble polymers called humins that are a waste byproduct.

It appears that two major industrial groups may have overcome these issues and are forming ventures for 2,5, FDCA commercialization.

- a) Synvina – a joint venture between BASF and Avantium.
- b) ADM (Archer Daniels Midland) and DuPont

It should be noted that many of the patents associated with the Synvina venture are listed under Furanix Technologies BV.

The patent literature for both ventures indicate that the second step is done under conditions that are similar to p-xylene oxidation to terephthalic acid in terms of reactor design, solvent and catalyst system and so using TPA process knowledge from the open literature should help simplify the study for the second step.

Both groups involve large, integrated, research capable companies; so, it is expected that both will succeed in their efforts.

The Synvina venture seems to draw on process knowledge from both partners:

- a) BASF – HMF step  
The evolution in their thinking can be seen in US Patents 8,952,186; 9,156,802; 9,162,998; 9,169,227; and finally summarized in 9,260,402
- b) Avantium – FDCA step  
The evolution of their thinking can be seen in US Patents 8,519,167; 8,865,921; and 9,643,945. Unfortunately, the patents only show experiments with 100% conversion and so whether the residence times were excessive and hurt selectivity cannot be resolved. Again, remember that the conditions are similar to the standard TPA process and so understanding the TPA process will be helpful to the analysis.

The ADM/DuPont venture seems to be heavier in ADM patents. The latest ones are:

- a) HMF Step - US Patents 10,017,486 and 9,776,980.
- b) FDCA step - US Patents 9,957,224 and 9,586,923



The patent literature for the Synvina venture appears to be richer for use in your analysis based on a cursory review. It seems that their patents provide the most clarity on process parameters needed to size the equipment and calculate OPEX. That being said, it is also worth looking at the ADM/DuPont literature to make sure that the cursory review was correct.

### **Design Basis and Processing Alternatives**

You should assume a plant capacity of 200,000 kiloton/yr of TPA in the crude mixture so that you are competitive to the scales of typical terephthalic acid plants.

You will need to determine the best reaction parameters for each step of the process. Since there are multiple reaction steps, you should explore various configurations of the facility to determine the most economic design. While your focus is on a crude product, you should try to produce as pure a crude product as possible to simplify the final purification and minimize its cost.

It is expected that sustainable FDCA will not be cost competitive with petrochemical based TPA. Therefore, a pricing premium will be required. You are to determine what market premium or subsidy is needed to have your 2, 5 FDCA market competitive. Your company requires a minimum 15% IRR on this venture to move forward. The marketing organization would like you to “bracket” the needed premium. Therefore, you are to study two cases;

- a) The IRR and NPV for a case where the 2,5, FDCA is sold at equivalent TPA market prices (remember the MWs differ).
- b) A 15% IRR case where the pricing premium is included. The marketing organization wants to know the magnitude of the premium and the resulting project NPV.

## 5. Culture Derived Human Platelets for Clinical Transfusion (Recommended by Prof. Scott L. Diamond, UPenn)

Human platelets are continually obtained from blood donors via whole blood donation or plateletpheresis for use in transfusion medicine. Unfortunately, they need to be stored at room temperature with gentle agitation, which means they have a short shelf life of just 4-5 days. Thus, the supply of platelets in a community is always 1 or 2 days away from a shortage. Mass trauma situations also stress community supplies. The laboratory production of culture derived human platelets using bioreactors would have great societal benefit. Platelet concentrate from whole blood donation provides  $5.5 \times 10^{10}$  platelets in 45-65 mL of plasma. Plateletpheresis provide  $3 \times 10^{11}$  platelets in 200 mL of plasma (1 Unit).

- 1) Consider ABO compatibility needs for cultured derived platelet transfusion.
- 2) Design a process that uses a source stem cell that can be continually cultivated. Various sources of cells to choose from are: human embryonic stem cells (hES), human induced pluripotent stem cells (iPS), continually renewable human hematopoietic stem cells (HSC), or a transdifferentiated HSC.
- 3) Design a process to differentiate your source stem cell to high ploidy megakaryocyte
- 4) Design a process using microfluidics or wave reactor or stirred bioreactor to create proplatelets and platelets. Consider fluid mechanics, scalability, product heterogeneity and overall economics of the venture in your design and decision of which technology to take forward.
- 5) Define all components for storage, use of plasma, packaging, sterility, and quality control testing.
- 6) Determine the cost and bioreactor scale on a per platelet bag and for a 1-million population metropolitan area.
- 7) Estimate the NPV and IRR for a venture located in a 1-million population metropolitan area in two ways: including and excluding the R&D and FDA costs to bring culture-derived human platelets to market.

### References

- 1) Thon JN, ..., Neeves KB, Weitz DA, Italiano. Platelet Bioreactor-on-a-chip. *Blood* 2014;124:1857-67
- 2) Ito Y, ..., Nishimura S, Eto K. Turbulence activates platelet biogenesis to enable clinical Ex Vivo Production. *Cell* 2018;174:636-648.
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## **6. Production of Single Cell Protein and Astaxanthin Using Methane as Carbon Source (recommended by Jeffrey D. Cohen, Janssen Biopharmaceuticals Division of Johnson & Johnson)**

A process has been developed for the commercial production of a high-quality, single cell protein and astaxanthin based on natural gas, more specifically methane. The process is based on the use of genetically-engineered methanotrophic bacteria, with the ability to utilize methane as the energy and carbon source in a fermentation process. A reactor has been developed which gives a very high mass transport of the gaseous raw materials into the water phase. Ammonium hydroxide is added to the process to control pH and as a nitrogen source for protein production. The final single cell protein product contains a large percentage of high-quality protein in terms of its amino acid profile. Feeding trials with salmon have shown that this product can be added up to an inclusion level of 20% of the total salmon feed replacing more than 50% of the fish meal, resulting in an equal or improved growth rate for the salmon compared with standard diets. The product may also be included in feed for other aquaculture species or livestock raised for dietary protein.

Astaxanthin is a 40-carbon carotenoid that provides pigmentation and antioxidant activity to fish and crustaceans grown via aquaculture. When astaxanthin is added to aquaculture feed as a substitute for pigment found in fish meal, salmon and shrimp exhibit coloration similar to those caught in the wild.

The process economics favor operating the bioreactor in the continuous phase. This involves removing a portion of the process suspension, separating the solids, and returning the liquid to the bioreactor in a sterile-state. The separated solids require drying to prevent product decomposition and to enable efficient packaging, storage, and transportation. The bioreactor will require feeds to provide essential growth components, water make-up, and foam control.

The bioreaction is aerobic and the enthalpy-of-fermentation must be managed with cooling to maintain the process temperature. Carbon dioxide is generated as a by-product and the bioreactor must be vented to avoid over-pressure and limit CO<sub>2</sub> accumulation.

Site location plays a key role in the process economics. The manufacturing may take place where stranded-gas is otherwise flared and may be considered to be free. The natural gas may be used in part to fuel on-site power generation for utilities, air-fractionation or ammonia production if so desired, as well as to provide the bioprocess carbon source.

Note that natural gas is a combination of methane, ethane, propane and higher alkanes. A separation process is needed to isolate methane from natural gas prior to feeding the bioreactor. You will need to account for the CAPEX and OPEX of, for example, a Pressure Swing Adsorption step to isolate methane from the other components in natural gas. Otherwise, if raw (whole) natural gas is fed to the bioreactor, the microorganisms will convert the higher alkanes to organic acids which will slow, or stop, cell growth.

The objective of this project is to determine the cost of manufacture of both products and the NPV and IRR of the overall project, by specifying the details of:

- the upstream, process equipment capable of growing single cell protein (SCP)
- the separation equipment capable of isolating a concentrate of SCP from the supernatant liquid
- the downstream process equipment capable of drying the SCP
- the sterilization equipment, needed to return supernatant liquid to the process, contamination free

- the equipment for separating and purifying the coproduct astaxanthin
- the packaging equipment capable of containing the dried SCP and astaxanthin 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.

Process details:

- annual production rate: 8,800 metric tons
- cell doubling time at maximum growth rate: 1.5 hours
- peak cell density in bioreactor (bone dry basis): 35 grams/Liter
- astaxanthin concentration: 0.3 wt.% of biomass on a bone-dry basis
- enthalpy of fermentation: -23.9 Kilojoules/gram SCP
- bioreactor campaign period in continuous, sterile operation: 6 weeks
- dried biomass, packaged bulk density: 0.7 Kg/Liter
- 95% process uptime

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

**References**

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6. U.S. Patent 4,048,013 A
7. US Patent 7,579,163 B2 Method of Fermentation
8. US Patent 4,048,013 Process for Producing Single-Cell Protein from Methanol using *Methylomonas* sp. DSM 580
9. U.S. Patent 9,617,575 High concentration methanol tolerant methanotroph and its application
10. U.S. Patent 4,795,708 Novel bacteria and single cell protein production therewith
11. U.S. Patent 4,166,004 Process for the preparation of single cell protein using *Methylmonas clara* ATCC 31226
12. U.S. Patent 4,106,988 Method of cultivating *Methylomonas* probus on methanol containing medium
13. U.S. Patent 4,048,013 Process for producing single-cell protein from methanol using *Methylomonas* sp. DSM 580
14. U.S. Patent 3,994,781 Process for the production of protein
15. Liu, W.C., et.al., Scaling up Fermentation of *Pichia pastoris* to demonstration scale using new methanol feeding strategy and increased air pressure instead of pure oxygen supplement, Nature, 21 January 2016, <https://www.nature.com/articles/srep18439.pdf>

## 7. Process Intensification using Dividing Wall Column (Recommended by Adam A. Brostow, UOP)

900 MM SCFD of natural gas is separated into components. The feed composition in mole fractions is given in Table 1.

**Table 1**

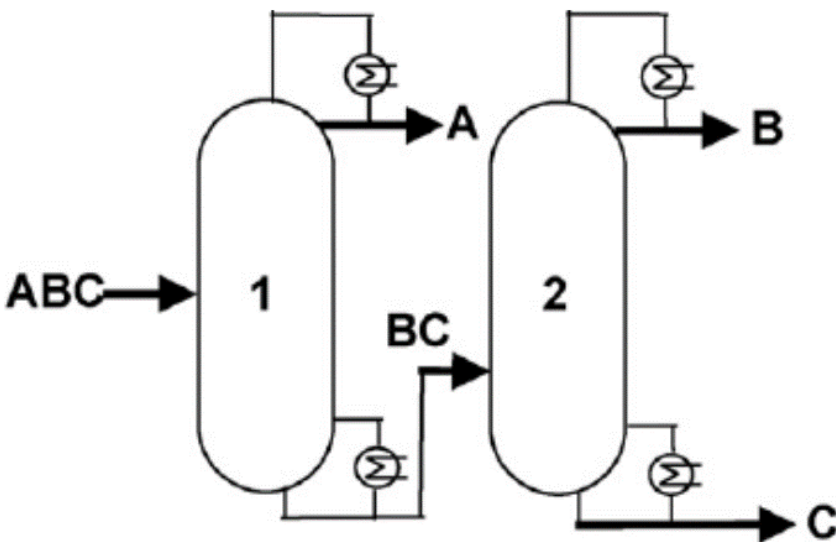
C1	0.9
C2	0.06
C3	0.02
I4	0.005
C4	0.005
I5	0.005
C5	0.0025
C6	0.0025

All methane (C1) and 90% of ethane (C2) are recovered as residue gas. The remaining 10% of C2 and heavier components (C3+) end up in natural gas liquid (NGL) product, the feed material for the process under consideration.

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. Note that I5 is isopentane, C5 is n-pentane, and C6 is n-hexane.

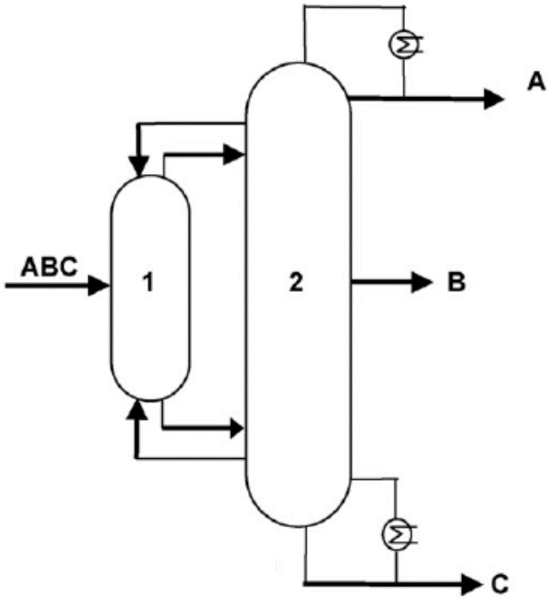
NGL is at 80 °F, 300 psia. The conventional fractionation system is a direct 2-column sequence shown in Fig. 1.

Fig. 1



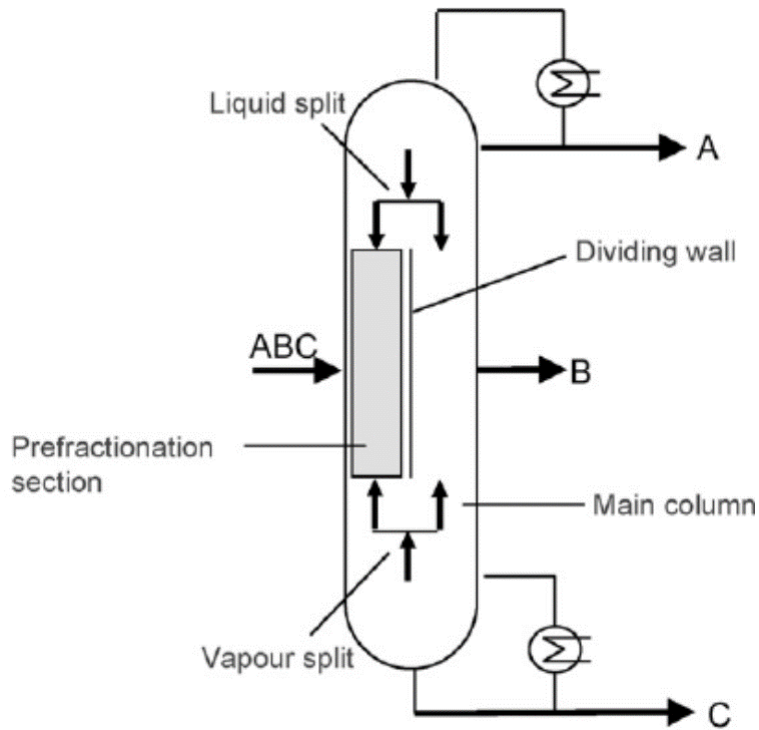
To potentially improve efficiency, one can use a fully thermally-coupled configuration, the so-called Petlyuk configuration, shown in Fig. 2

**Fig. 2**



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

**Fig. 3**



## **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  $-40^{\circ}\text{C}$  or  $F$ ; it's up to you to choose units). The limitation is the NBP of propane refrigerant used as the cold utility.

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 team will simulate the direct sequence (as a benchmark) and DWC (tip: it can be simulated as two columns with two recycles or as four columns) and compare CAPEX and OPEX.

Bear in mind that the deethanizer (DEC2, first column in the direct sequence) and single DWC condensers will operate below ambient and will require mechanical refrigeration, part of CAPEX and OPEX. DELPG column's (2<sup>nd</sup> column in direct sequence) condenser is at no less than  $80^{\circ}\text{F}$  (ambient cooling).

There is no need to simulate mechanical refrigeration or NGL extraction from natural gas.

The problem seems simple but will require good understanding of distillation and significant simulation skills. Students are encouraged to suggest improvements and modifications such as heat and power integration, intermediate reboilers or condensers, or heat exchange combined with distillation (e.g. dephlegmators).

## **Note**

The author of this project is not based in Philadelphia. Many or all interactions with the author will be through SKYPE, phone and/or email. Before leaving Air Products and Chemicals in Allentown, PA, over many years, the author provided many excellent design projects for CBE 459 design groups and was an active design consultant.

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Realize the Potential of Process Intensification, Bielenberg et al., CEP, 2018

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Reduce Costs with Dividing-Wall Columns, Schultz et al., CEP 2002

Are Thermally Coupled Distillation Columns Always Thermodynamically More Efficient for Ternary Distillations? Agrawal et al., 1998

Rules of Thumb for Chemical Engineers by Branan

## **8. Air to Fuels Production Facility (Recommended by Stephen M. Tieri, DuPont)**

Conventional liquid fuels have been, and continue to be, an integral part of modern society. As a result of climate change, dwindling petroleum resources, material pricing volatility, and 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. The disposition of agricultural resources and production to support both this transition from petroleum to renewable fuels and provide food to meet the demands of the increasing global population is a source of controversy and significant discussion. 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.

One new technology, developed and piloted by Carbon Engineering (CE), has attracted significant attention in the news, online articles, and scientific journals (The New York Times, Boston Globe, Bloomberg, Joule, and International Journal of Greenhouse Gas Control Technologies, to name a few). The AIR TO FUELS™ technology and process is advertised as directly synthesizing transportation fuels – such as gasoline, diesel, or jet fuel using only atmospheric CO<sub>2</sub> and hydrogen split from water, and powered by clean electricity. The technology is presented as a tool to significantly reduce the carbon footprint of the transportation sector by recycling atmospheric CO<sub>2</sub> into liquid fuel and displacing crude oil. Additionally, the process offers an avenue to avoid the infrastructure turn-over of hydrogen fuel cells, and the land use and food security problems associated with traditional biofuels.

The AIR TO FUELS™ process is promoted as having the capability to produce synthetic drop-in compatible fuels for less than \$1.00 /L at commercial scale, effectively being cost competitive with current biodiesel pricing. The AIR TO FUELS™ process has potential to deliver fuels that have an ultra-low life-cycle carbon intensity, or that are fully carbon neutral (depending on the energy source used to power the Direct Air Capture (DAC) component of the process).

At a high level, the process as envisioned has three major steps: 1) extracting/capturing CO<sub>2</sub> to produce a feed stream, 2) extracting/producing a hydrogen feed stream, and 3) processing the hydrogen and carbon dioxide containing streams to produce a synthetic fuel. More specifically in the most desired and advertised embodiment of the technology, the CO<sub>2</sub> is extracted from air and hydrogen is generated via water electrolysis powered by solar cells.

Beginning in 2015, CE has completed successful pilot testing of the CO<sub>2</sub> capture technology; and in 2017 initiated liquid fuel production at pilot scale. With pilot process testing expected to be completed after two years, CE is actively seeking strategic partners to build full-scale commercial AIR TO FUELS™ facilities, and customers interested in supply agreements for ultra-low carbon fuel.

Your company maintains a significant presence in the fuels industry, is actively interested in augmenting their portfolio with renewable and financially attractive technologies, and envisions building and operating the 1<sup>st</sup> commercial scale AIR TO FUELS™ facilities to sell the liquid fuel products.

Your project team has been assembled to design the first commercial plant for this new sustainable technology, and determine if it is commercially viable at a 2000 bbl/day capacity for any combination of gasoline, diesel, and jet fuel. It is critical to identify which, if any, combination of facility locations, fuel products, fuel standards, regulatory requirements, and/or CO<sub>2</sub> taxes/credits is necessary for commercial viability. Specific facility and product sales locations for economic and financial assessment are California, Germany, British Columbia (Canada), and Pennsylvania. Your team is also responsible for



identifying and minimizing the required investment and operating costs, optimal product mix, and identifying any critical economic sensitivities to raw materials, product mix, utility, or equipment pricing.

The plant design should be as environmentally friendly as possible, at a minimum meeting state and federal emissions requirements. 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.

## **References**

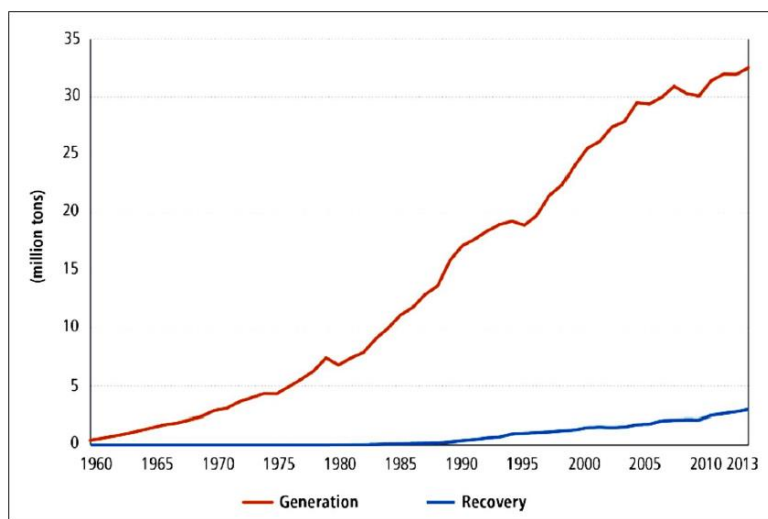
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## 9. Chemical Recycling of Plastics by Dissolution (Recommended by Dr. Matthew Targett, SpruceWorks LLC)

### Overview

Plastic items are a critical part of modern society and they are used in almost every aspect of our lives. One of the values of plastics for packaging and as manufactured articles is their inherent strength and durability. However, this means that plastics remain durable after use and continue to accumulate in the environment indefinitely. As we use more and more plastic, we also discard an ever-growing amount of plastic that will last for centuries.

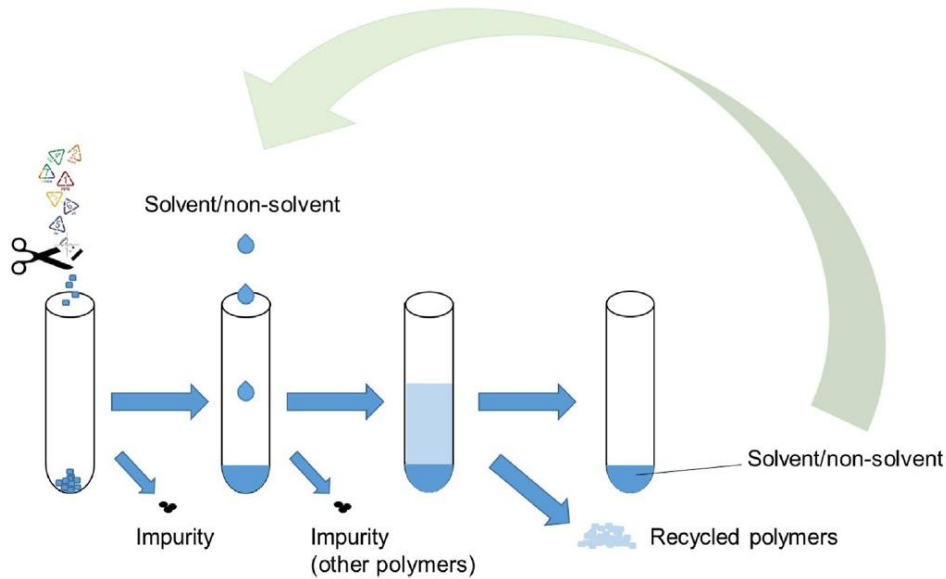
Today, plastics are disposed of in several ways including recycling, landfilling, incineration, composting and littering. In the US, nearly 90% of plastics are being discarded into landfills. To be more sustainable, it is important to understand what our environmental and economical options are for waste plastic recycling and embrace techno-economically viable methods that will address these issues.



### Plastics Generation and Recovery via Recycling

Source: US EPA

Dissolution and reprecipitation of plastic wastes has been considered for a number of polymer types over the past several decades as a means of reconstituting and purifying the polymeric feedstock material. See [1] Zhao et al., 2018 where the following schematic is reported.



**Schematic Drawing of the Dissolution/Precipitation Technique.** Source: [1] Zhao et al, 2018.

	Solvent extraction	Primary mechanical recovery
Procedures	<ol style="list-style-type: none"> <li>(1) Cut and remove the pollutant and impurity.</li> <li>(2) Dissolve to the highest possible concentration.</li> <li>(3) Re-precipitate the polymer in solvents by adding nonsolvents (add supercritical fluids to extract solvents)</li> <li>(4) Filter, wash, and dry the obtained polymer</li> <li>(5) Separate and recover solvent/nonsolvent (solvent/supercritical fluids).</li> </ol>	<ol style="list-style-type: none"> <li>(1) Shred (grind) plastic in a suitable form</li> <li>(2) Wash the plastics by water</li> <li>(3) Agglutinated by pigments and additives</li> <li>(4) Extrusion</li> <li>(5) Quenching</li> <li>(6) Granulation</li> </ol>
Advantages	<ol style="list-style-type: none"> <li>(1) Obtained in accepted form, such as granules and powder.</li> <li>(2) Remove the additives and insoluble contaminants.</li> <li>(3) No further degradation occurs except heating for a fully dissolution.</li> <li>(4) The properties of the recycled product are competitive compared with virgin products.</li> <li>(5) A massive decrease in the bulk volume.</li> </ol>	<ol style="list-style-type: none"> <li>(1) The properties of the recycled product are competitive compared with virgin products.</li> <li>(2) Simple operation</li> </ol>
Disadvantages	<ol style="list-style-type: none"> <li>(1) Relatively high technical requirements</li> <li>(2) Relatively high costs</li> </ol>	<ol style="list-style-type: none"> <li>(1) Degradation of recovered product</li> <li>(2) Limited applications</li> </ol>

**General Comparison of Dissolution/Precipitation Technique with Primary Mechanical Recovery Technique.** Source: [1] Zhao et al., 2018.

For the purposes of this project, the objective will be to determine the optimal commercial dissolution-precipitation process configuration for converting waste polyethylene (PE) to useful recycle polymer products. It is recommended to base the main conversion process directly on the experimental data reported in [2] Pappa et al, 2001 or [3] Achilias et al, 2009. If any other new work involving super critical CO<sub>2</sub> as the reprecipitation solvent is found in the literature, then it should also be considered as a viable alternative for comparison.

- Dissolution-Reprecipitation of waste PE shopping bags (customer drop off at stores such as Walmart, other)
- Temperature ranges and residence times for Dissolution and Reprecipitation and Drying as indicated, but challenge the kinetic rates of these processes which may be improved based on accepted industrial practices.
- Product Outputs: mainly purified PE, and also non-PE residue (inks, other plastics, paper, tramp materials, etc.)

Polymer	Strong solvents	Weak solvents	Experimental conditions	References
PE	xylene	propanol	30 L xylene was added into a mixture of 3 kg PE and 3 kg PP with stirring for 1 h at 85 °C, and PE was dissolved, precipitated by 90 L propanol, and dried at 80 °C for 6 h.	(Pappa et al., 2001)
PE	xylene	n-hexane methanol	1 g PE was dissolved in 20 mL solvent with heating (100 °C) for 30 min, reprecipitated, and dried at 89 °C for 24 h.	(Achilias et al., 2009b)

**Example Dissolution-Reprecipitation Schemes**, from [2] Pappa et al 2001, and [3] Achilias et al 2009.

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, dissolution, filtration, solvent recycle, reprecipitation, filtration, reprecipitation solvent recovery (drying), and recycle polymer pelletization. The main refining steps of solvent(s) recovery need to take into account integrated energy saving heat integration schemes. 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

- Capacity: 50 TPD PE waste bag feed
- Polymer Product Purity, polymer grade purity of >99.99%
- Polymer selling prices, to be estimated by analysis of long term market trends
- Waste polymer purchase costs, assume small nominal payment (as this material may be sent to landfill currently at a cost to the retailer)
- Waste polymer delivery costs, assume market based shipping fees

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

- Types of solvent recovery systems (filters, dryers, distillation, etc.)
- Process temperatures (dissolution, reprecipitation, drying, etc.)
- Heat integration

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 annual PE consumption
- IRR/NPV

## Note

The author of this project is not based in Philadelphia. Many or all interactions with the author will be through SKYPE, phone and/or email. Over many years, the author has provided many excellent design projects for CBE 459 design groups and has been an active design consultant.

## References

- [1] Zhao, Y.B. et al; **Solvent-based Separation and Recycling of Waste Plastics: A Review**. Chemosphere, 209: 707 -720, 2018
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## **10. Future API Manufacturing Excellence (Recommended by Alex Marchut, Janssen Biopharmaceuticals Division of Johnson & Johnson)**

### **Background: Lyophilization**

Freeze-drying (lyophilization) is a process extensively used in industry to stabilize active pharmaceutical ingredients (API), particularly for large molecules. It is an expensive, time- and energy-intensive process that is often run far from optimal conditions [1]. A main root cause for this is the fact that API availability during early process development is an issue, while barriers for improvements later on – when API is more readily available – are high. The cost of performing an experimental study in the form of, e.g., a Design of Experiments (DoE), is often deemed to be unacceptable, given the internal and external (regulatory) hurdles for process changes and the fact that the gain could be minimal (in the unlikely case the process is already run at the optimum).

### **Background: Fluid Bed Granulation**

Fluid bed granulation is a common processing step in manufacturing of small molecule pharmaceutical drug product. The ingredients can be granulated and dried in the same step, reducing material handling and shortening process times. Additionally, fluidization is efficient at drying the product when compared with other wet granulation processes [4-6]. Granulated materials are desirable and enable common downstream processing of small molecule drug product in the following ways. They have improved flow characteristics and compressibility which can be important for efficient and reproducible tablet compression. Granulation also reduces or eliminates the propensity for segregation hence improves content uniformity and reduces dust, improving operator and environmental safety [7]. A fluid bed granulation process has four input process parameters that will impact the output granules – spray rate, air temperature, air flow rate, and air humidity. Of these, you can control all except air humidity, which can vary from 1 g/kg to 10 g/kg absolute.

### **Project Statement**

You are a sub-team of “Future API Manufacturing Excellence” (FAME), a strategy group within a major pharmaceutical company, which is focused on developing business cases for potential high-impact technologies. You have partnered with another, internal group who has come up with a mathematical model of a crucial part of the lyophilization process, the ‘primary drying’ step, which allows you to simulate key characteristics, such as the drying time and maximum product temperature (a feature related to quality) in silico. They have also created a mathematical model of the fluid bed granulation process, which allows you to simulate it and get the drying time (note that the spraying time will depend on the solution quantity, which is fixed, and the spray rate, which you should optimize) and maximum product moisture (which is related to product quality). You will be given access to the model and required to stay within the maximum product moisture design space as you optimize the granulation. You will be given access to both “black box” models.

For lyophilization, your objective is to design a faster and/or cheaper process that satisfies all constraints (product quality and equipment capability) for a new compound, HAJVANOX, for which the existing process is suspected to be suboptimal. The cost calculation obviously should include items such as the energy cost associated with the low pressures and temperatures.

For fluid bed granulation, your objective is to optimize the granulation of a high-volume product, Botilioxin. Your goal is to find a global optimum in cost of running the fluid bed granulator considering the energy cost of heating and blowing the air, the electricity required to pump the spray, the depreciation of the equipment, labor cost, etc.

For both processes, the cost estimates should also include things like, labor, depreciation of equipment etc. and the outcome should be compared to the current base case processes which will be supplied to you.

Specifically, you should calculate the change in NPV for your design for lyophilization compared to the base case, and for fluid bed granulation compared to its base case. If your design involves additional capital expenditures beyond the base case design, calculate the incremental IRR on that incremental investment. You should also study the sensitivity of the business cases towards external factors such as the demand forecast, raw material cost, retail price of the final product, etc.

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## 11. Conversion of Omega-3 Fatty Acids from Algae Biomass to Biodiesel (Recommended by Leonard A. Fabiano, Geetanjali Yadav, and Warren D. Seider, UPenn)

After extraction of triglyceride oil from microalgae, Zhu et al. (2017) designed a plant to produce omega-3 fatty acids, which provide significant health benefits, improving heart and mental health. Then, a new intensified process to produce commodity quantities of biodiesel from microalgae (Yadav et al., 2018), especially used as transportation fuel, also produced omega-3 fatty acids as a co-product, which are useful as infant food and animal feed. Moreover, because excess quantities of omega-3 fatty acids are produced, they can be converted to biodiesel fuel via a reaction path that uses ultrasonic energy for the transesterification process (Armenta et al. 2007). This way, a biorefinery is established from CO<sub>2</sub> sequestered algal biomass to produce fuel, feed, and nutraceuticals using an intensified process.

The hydrothermal liquefaction (HTL) process (Bidy et al., 2013; Anderson, 2013), designed by the DOE Pacific Northwest National Laboratory (PNNL), operates at temperatures (350°C) and pressures (200 bar) too high to produce health supplements. A key advantage is that 65 wt% of the algae carbon is converted to transportation fuels. But, the intensified process (Yadav et al., 2018), because it operates at just 90°C and much lower pressures, introduces a new flexibility to produce quantities of omega-3 fatty acids as co-products of the main biodiesel fuel product. The remainder can be converted to biodiesel using the Armenta et al. (2007) transesterification.

As microalgae species contain different types of triglycerides (carbon chain-length and saturation), different kinds of products may be expected from the same strain depending on various process and culture conditions (Vazhappilly and Chen, 1998). This design project involves adjusting and improving (replacing the ball mills and hexane extraction with microbubble extraction) in the Zhu et al. (2017) plant and, for adjustable quantities of residual algae biomass, designing a plant using the Armenta et al. (2007) transesterification. The intent is to design a plant that provides the flexibility to adjust, within limits, the amount of residual algae biomass to be transesterified, depending on consumer demand for the bio(co)products. Given the relatively high prices of omega-3 fatty acids and animal feeds, a key question involves whether the combined processes produce biofuels, and these bio(co)products, less expensively than the HTL process. If so, it will be recommended that a pilot-plant design be undertaken to demonstrate the feasibility of these combined processes.

Stated differently, the student design team will decide upon the size of the plant and the coproduct slate to maximize the economic viability of the project, while allowing flexibility for adjusting the product slate depending on then-current customer demand (prices).

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